

**SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYIMIDE GAS
SEPARATION MEMBRANE MATERIAL SYSTEMS**

by

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(ABSTRACT)

Phenylindane monomers 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI), 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane (TAPI) and 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI) were synthesized and characterized. DAPI, as well as other diamines, were then utilized in solution step polycondensation with a number of commercially available dianhydrides using either the two-step ester-acid solution imidization or the high temperature solution imidization routes. High molecular weight soluble fully cyclized polyimides were successfully synthesized using a 1:1 molar ratio of dianhydride to diamine. The polyimides were film forming and were characterized by size exclusion chromatography (SEC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and selective gas permeation methods, as well as other techniques. The O₂ permeation and O₂/N₂ selectivity values obtained for materials prepared in this thesis are discussed in relation to the concept of an “upper bound”, as defined in the literature concerning gas separation membranes.

The series of polyimides based on DAPI and several dianhydrides were found to have high glass transition temperatures (247°C-368°C) and very good short-term thermal stability as shown by TGA, despite the partially aliphatic character of DAPI. The 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione (6FDA)/DAPI system also exhibited low weight loss under nitrogen at 400°C, which was comparable to that of a wholly aromatic polyimide based on 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA)/4,4'-oxydianiline (ODA) which is known to have high thermal stability. In addition, the 6FDA/DAPI polyimides had a refractive index value of 1.571 from which the dielectric constant was calculated, giving an attractively low estimated value of 2.47.

The rigid, bulky and isomeric structure of DAPI in the repeat unit imparted film forming characteristics that allowed production of solvent cast membranes which displayed a range of O₂ permeability and O₂/N₂ selectivity characteristics. High O₂ permeabilities were observed for polyimides in which the DAPI structure predominated in relation to the overall polymer repeat unit, i.e. in combination with low molar mass dianhydrides. The more flexible dianhydrides afforded a greater degree of molecular freedom and were thought to result in a more tightly packed polymer conformation which decreased the rate of gas penetration through thin films. The DAPI/3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) system showed the best combination of O₂ permeability and O₂/N₂ selectivity values (2.8Ba and 7.3, respectively). Modest variations in the DAPI isomeric ratio did not significantly effect the gas permselectivity properties.

High molecular weight polyimides based on DAPI and BTDA were synthesized by three different routes. The ester-acid and thermal imidization methods produced polyimides with the highest T_gs and best thermal stability in air, as compared to the chemical imidization procedure. For example, a T_g increase of 22°C and a 68°C increase in the 5% weight loss were found for the ester-acid imidized DAPI/BTDA polyimide over those found for the chemically imidized version. The higher T_g and 5% weight loss values were attributed to the elimination of residual uncyclized amide acid moieties.

Polyimides derived from 6FDA were synthesized by the high temperature solution imidization method. Thin films, cast from NMP, were tough and creasable and afforded high T_g (>295°C) systems with good thermal stability. When combined with rigid diamines, 6FDA contributed to high O₂ permeation and moderate O₂/N₂ selectivity. The high O₂ permeability was ascribed to hindered interchain packing attributed to the bulky CF₃ groups. The exceptionally high oxygen permeability and O₂/N₂ selectivity values of the 9,9-bis(4-aminophenyl) fluorene (FDA)/6FDA system, were near the desirable “upper bound” for gas separation membrane materials, while those of 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)/6FDA were actually above the upper bound.

High performance polymers based on 4,4'-bis [4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPEDA), 2,2'-bis [4-(3,4-

dicarboxyphenoxy)phenyl] propane dianhydride (BPADA), 2,2-bis(3-amino-4-methylphenyl)hexafluoroisopropylidene dianhydride (Bis-AT-AF) and 3,7-diamino-2,8-dimethyl-dibenxothiophene-5,5-dioxide (DDBT) were also synthesized in this work. Additionally, they were characterized with regard to molecular weight, glass transition temperature, and thermal stability.

Polyimide systems containing hydroxyl moieties in the repeat unit were also investigated. Incorporation of hydroxyl moieties in the repeat unit enhanced chain stiffness via intermolecular hydrogen bonding and showed T_g increases of $\sim 30^\circ\text{C}$. Hydroxyl moieties also decreased the thermal stability values typically observed for polyimides. High O_2/N_2 selectivity was achieved with all of the 4,4'-diaminobiphenyl-3,3'-diol (HAB) containing polymers. However, these materials also had low O_2 permeabilities, which suggested a tightly packed structure, possibly facilitated by hydrogen bonding. In contrast to suggestions in the literature, the comparison between a polyimide having pendant hydroxyl groups and another having the same repeat unit without them did not reveal a significant change in permselectivity behavior.

The synthesis, characterization and crosslinking behavior of functional polyimides containing phenol, amine and acetylene moieties are also described. A crosslinking reaction of oligomers containing phenol moieties with a tetrafunctional epoxy resin was achieved 100°C below the “dry” glass transition temperature and was attributed to residual solvent. Utilization of this crosslinking mechanism could allow membrane optimization by investigating the influence of a number of variables, such as the concentration of the phenolic moiety, epoxy weight percent, catalyst concentration and residual solvent content.

To my brother,
Matt,
whose life models sacrifice
for the promotion of others

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CHAPTER 1 RATIONALE AND OBJECTIVE

As the new millennium dawns, major new demands are required of the materials we use. Aromatic polyimides are a class of high performance polymers that have excellent thermal, electrical and mechanical properties. They are currently applied in many areas such as aerospace, microelectronic, automotive and gas separation industries as high-temperature coatings, structural adhesives, matrix resins, films, interlayer dielectrics, wire insulation and semipermeable membranes.

Further development of new polyimide systems and modification of existing systems are ongoing tasks to further enhance their desirable properties and applications. One area which has received considerable attention in recent years is selective gas permeation through polymer membranes. Gas purification by semipermeable membranes became economically competitive to cryogenic methods only in the late 1970s. The development of improved polymer material systems for this relatively new application is of great interest.

Commercially viable materials must have both a high permeability and a high selectivity for the gas separations of interest. In recent years, the structure/permeability/selectivity relationships of polymers have become the objective of systematic studies in order to achieve these property characteristics.

The research in this dissertation has focused on the synthesis, characterization and permselectivity properties of high molecular weight, soluble polyimides. The primary interest was to design polymer repeat units, which would yield a highly permeable and highly selective membranes for the O₂/N₂ gas pair. This objective was accomplished by employing two methodologies. The first methodology was to design and investigate novel polyimide systems. Monomer selection was initially based on literature observations. The second methodology utilized monomeric hydroxyl-bearing diamines, which were expected to enhance chain stiffness via intermolecular hydrogen bonding, favorably influence permselective behavior and provide a crosslinkable site suitable for thin films or hollow fiber membranes.

In addition to high permselectivity values, membranes must also be chemically robust. Therefore, this research also focused on crosslinkable polyimides, which, under a given set of conditions, would afford a lightly crosslinked material and thereby increase solvent and contaminant resistance.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Polyimides are step or condensation polymers derived from both aliphatic or aromatic dianhydrides and diamines, or their derivatives, and contain a heterocyclic imide linkage in the repeat unit, as shown in Figure 2.1.

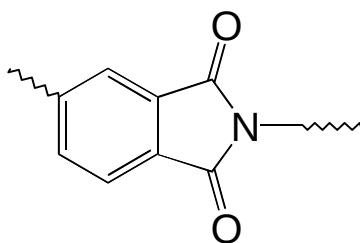


Figure 2.1 A Heterocyclic Imide Linkage

Polyimides are both scientifically and commercially important due to their excellent thermal stability and mechanical strength. Innovative polyimide design has led to their use in aerospace, microelectronics, automotive and packaging industries.

This chapter will discuss topics relevant to this dissertation, including synthetic chemistry, methods of polyimide preparation, polymer characterization, applications, gas separations theory, and structure/property relationships in gas permeation science.

2.2 Synthesis of Polyimides

The number of versatile synthetic methods for the formation of polyimides has facilitated their range of utility in high performance applications.¹⁻⁹ The prominent synthetic methods as well as some more novel routes to polyimide formation will be presented in this section.

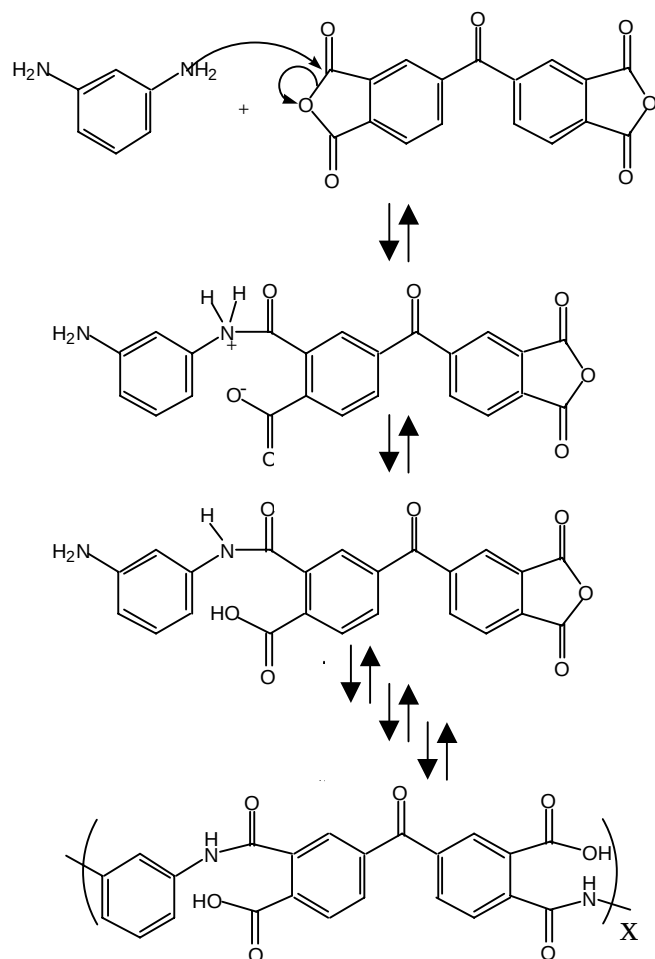
2.2.1 Classical Two-Step Method

2.2.1.1 Poly(amic acid) Formation

The most important method for polyimide synthesis has been the “two-step” method involving a polyamic acid (PAA) precursor, which is subsequently cyclized to form the imide linkage. This route is also known as the “classical” method. Many of the mechanistic pathways involved have been elucidated by a number of researchers over the past forty years.

Generally, the polyamic acid is formed when a difunctional amine and a difunctional anhydride mutually react in a polar aprotic solvent. This proceeds by a reversible nucleophilic substitution reaction when the amine attacks one of the carbonyl carbons in the anhydride moiety and displaces a carboxylate functionality, followed by proton transfer (Scheme 2.2.1.1.1). The reactivity and concentration of each of the monomeric units and the nature of the solvent will determine the rate of PAA formation and its stability with regard to other reagents.

Some typical dianhydrides and diamines are shown in Figure 2.2.1.1.1, along with their common acronyms. Dianhydride reactivity was found to best correlate with electron affinity (E_a) (Table 2.2.1.1.1),¹⁰ and thus, the dianhydride with the greatest electrophilicity, i.e. the highest electron affinity, will react first with a given nucleophile. As shown by E_a values in Table 2.2.1.1.1, PMDA is clearly much more reactive than the other anhydrides. The reason for the relatively high reactivity of PMDA and the range of dianhydride E_a s observed is the differences in electronic environment of the anhydride carbonyl groups which can easily be illustrated with BTDA, BPDA, and ODPA. BTDA is bridged by an electron withdrawing carbonyl group. By removing electron density through the pi-orbitals, the anhydride carbons experience a greater positive environment, which facilitate attack by a nucleophile. ODPA on the other hand is linked by an oxygen atom which is able to donate electrons into the ring thereby reducing the anhydride carbons' affinity for incoming electrons from an attacking nucleophile. In the case of BPDA, where no bridging functionality is present to either withdraw or donate electron density, an intermediate E_a value between BTDA and ODPA is observed.



Scheme 2.2.1.1.1 Isomeric Polyamic Acid Formation via Nucleophilic Substitution at an Anhydride Carbonyl

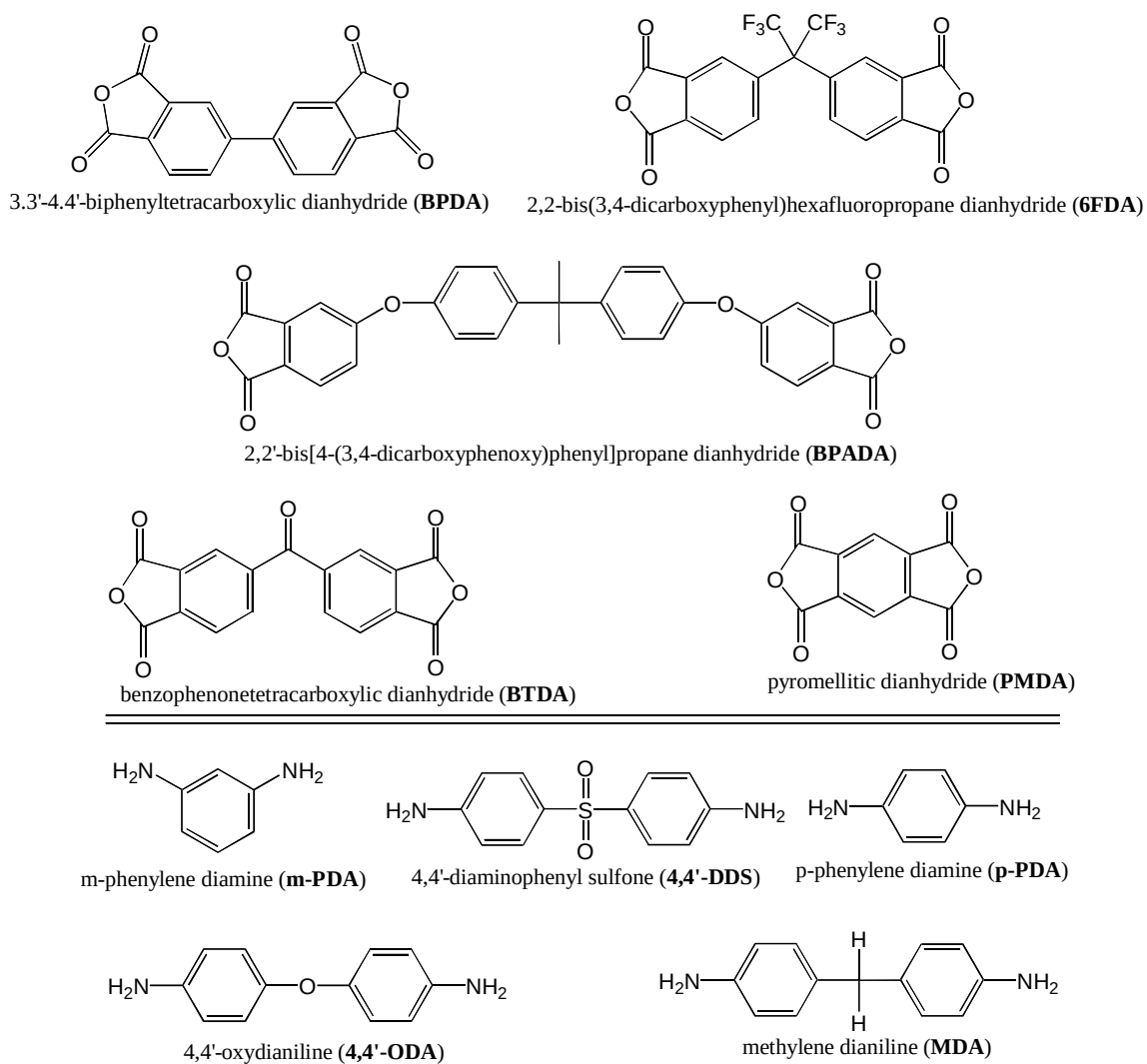
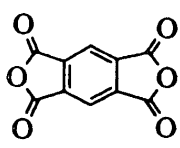
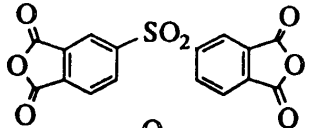
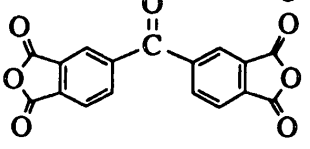
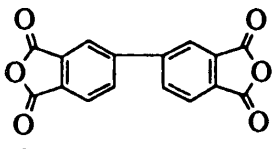
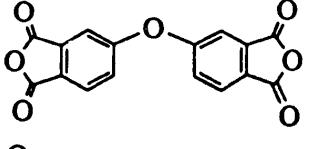
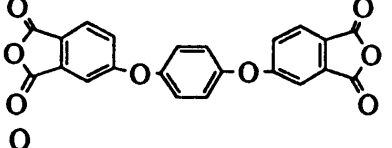
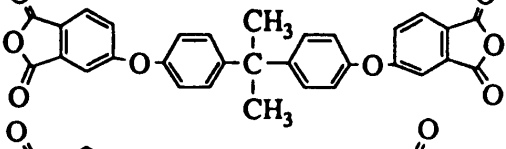
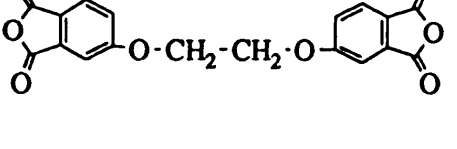


Figure 2.2.1.1.1 Common Dianhydrides and Diamines

Table 2.2.1.1.1 Electron Affinity of Representative Aromatic Dianhydrides¹⁰

Dianhydrides	E_a (eV)
	(PMDA) 1.90
	(DSDA) 1.57
	(BTDA) 1.55
	(BPDA) 1.38
	(ODPA) 1.30
	(HQDA) 1.19
	(BPADA) 1.12
	(EDA) 1.10

It is also known that when electron withdrawing and donating bridges are present, they will have greater influence on E_a when located para- or ortho- to the anhydride carbonyls.

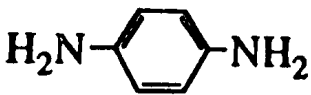
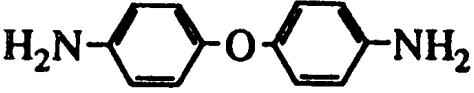
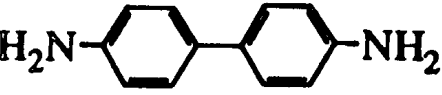
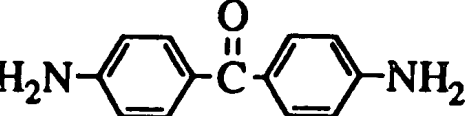
Diamine reactivity towards phthalic anhydride was found to correlate well with basicity pK_a (Table 2.2.1.1.2),¹¹ eg. an amine with a greater basicity will react faster. A diamine bridged by a withdrawing group, eg. diaminobenzophenone, shows decreased nucleophilicity.

When diamines and dianhydrides of low reactivity are used for PAA formation, a lower molecular weight would be expected when compared to a highly reactive diamine/dianhydride system,¹² assuming a fixed reaction time since X_n is directly dependent on $1/(1-p)$ (p = degree of polymerization).

From the discussion above, it is already apparent that the rate of PAA formation is largely dependent on diamine basicity and anhydride electron affinity. However, reaction rate is also a function of the solvent. The overall reaction involves a relatively weak base reacting with a non-protic anhydride to yield a strong protic acid. In general, this reaction is enhanced when a more basic aprotic solvent is utilized¹³ due to its favorable interaction with the strong acid (NMP>DMAc>acetonitrile>THF). In fact, it has been speculated by some that using a 4:1 ratio of DMAc or NMP allows complexation with each di(amic acid) repeat unit (Figure 2.2.1.1.2)^{14,15}, which could be a driving force for PAA formation. However, if the aprotic solvent is not basic enough it is possible that the strong acid formed may autoaccelerate the reaction and also shift the equilibrium away from high molecular weight PAA.¹⁶

It has been reported that diamines which are weak bases, such as 4,4'-diaminodiphenylsulfones, react slowly with BTDA in DMAc, but high molecular weights are rapidly achieved in THF.¹⁷ Two possible explanations for this are proposed. There may be a specific interaction between the amine and THF which increases its basicity and/or the THF may not be basic enough to deprotonate the acid to form the carboxylate, thus driving the reverse reaction.¹²

Table 2.2.1.1.2 Basicity pK_a of Diamines and Their Reactivity Towards 1,2,4,5-Benzenetetracarboxylic Dianhydride (PMDA)¹¹

Diamine	pK_a	$\log k$
	6.08	2.12
	5.20	0.78
	4.80	0
	4.60	0.37
	3.10	-2.15

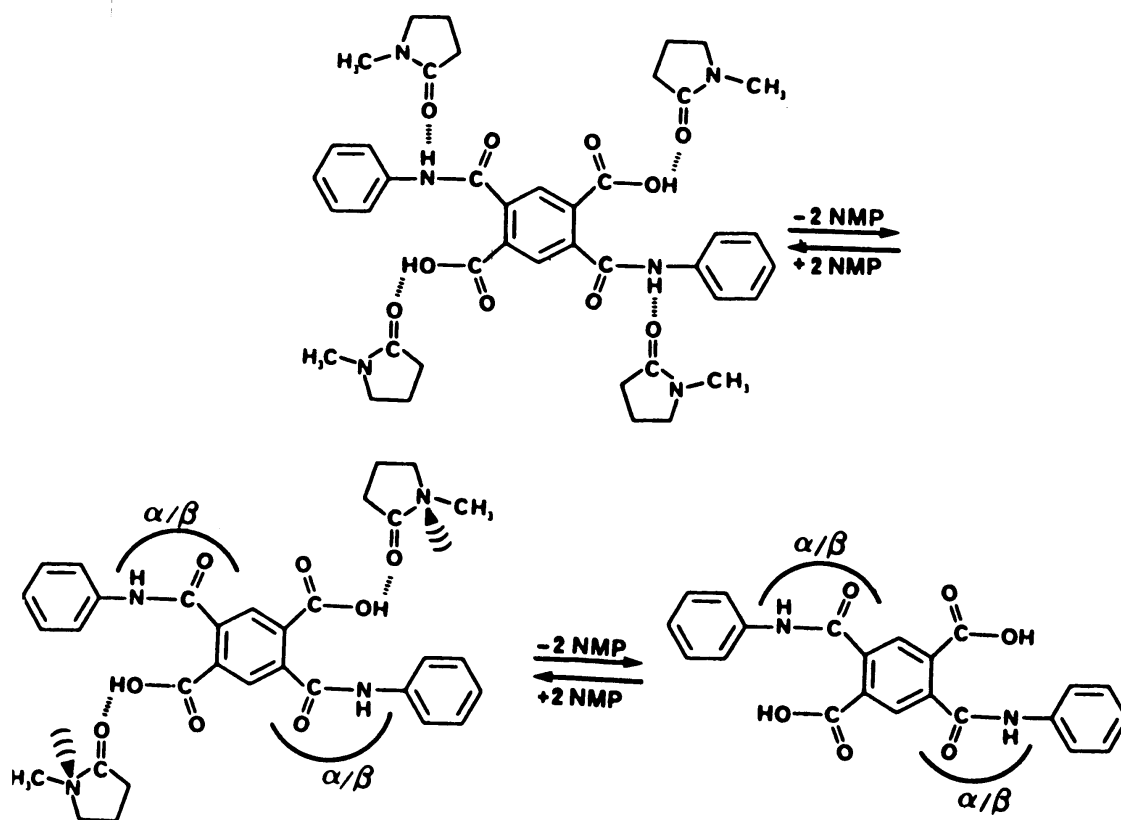
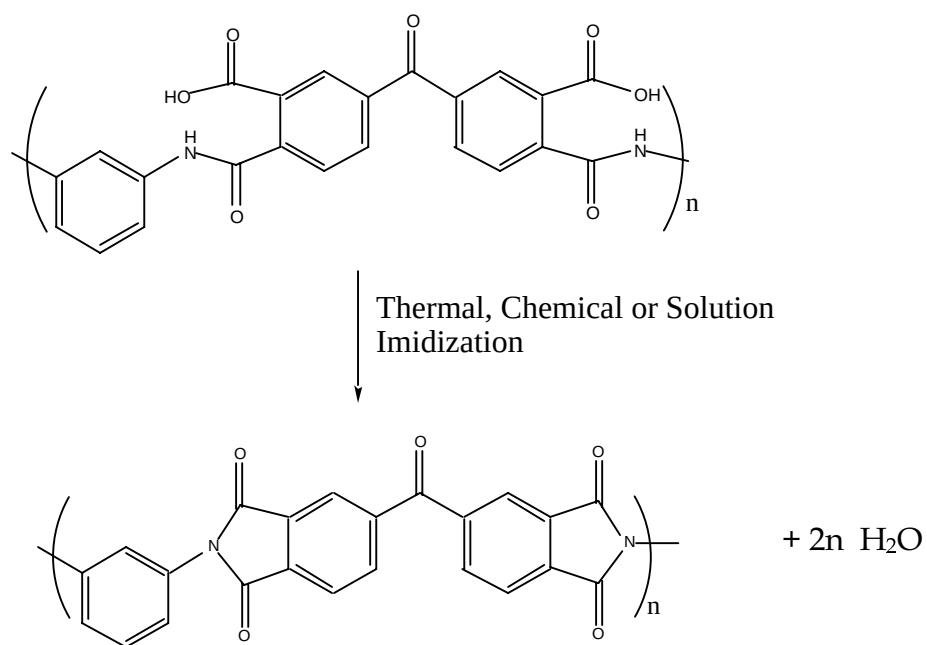


Figure 2.2.1.1.2 A Model for a 4:1 Ratio of NMP Complexation with a Di(amic acid)
Repeat Unit¹⁵

To enable formation of PAA having a well-defined molecular weight, it is imperative to completely remove water from the monomers and the reaction solvents. This is usually achieved by carefully drying the monomers and distilling the solvents. In the presence of water the dianhydride will hydrolyze to form the diacid which reacts at a much slower rate with a given amine. Water will also promote the reverse reaction, which is hydrolytic scission of the amide link. Cyclization of PAA will also generate water and may facilitate chain hydrolysis. Three methods have been employed to facilitate the cyclization of PAA and the removal of water. Cyclization and the removal of water can be achieved by either heating the PAA in solution or as a cast film, or it can be chemically induced through the addition of dehydrating reagents (Scheme 2.2.1.1.2).

2.2.1.2 Thermal (Bulk) Imidization

Polyamic acids, which may precipitate upon cyclization due to the increase in chain rigidity, are generally cast from solution and thermally imidized in a film form, which is also known as “bulk imidization”. Commercial examples of polyimides produced by this route include the Kapton family from DuPont (Figure 2.2.1.2.1). A widely employed¹ laboratory thermal cycle, conducted under vacuum or nitrogen to remove water and prepare bubble-free films is as follows: R.T. for one hour, 100°C for one hour, 200°C for one hour, and 300°C for one hour. Important features of the solid-state imidization reaction are still incompletely understood, including the influence of decreased molecular mobility and the effect of residual solvent.¹⁸ Although the mechanism is not well understood, it is thought to proceed by a nucleophilic substitution reaction involving the amide nitrogen and the ortho-carboxylic acid. The product of this reaction, water, is then thermally removed. This mechanism has been established for solution imidized systems and will be discussed later. The bulk reaction is known to be promoted by residual solvent. Not only does solvent plasticize the film, which allows greater chain mobility, but it also favors the appropriate conformation needed for cyclization to occur.¹⁴ An increase in chain mobility



Scheme 2.2.1.1.2 Three Common Routes to Facilitate the Conversion of Polyamide Acids to Polyimides

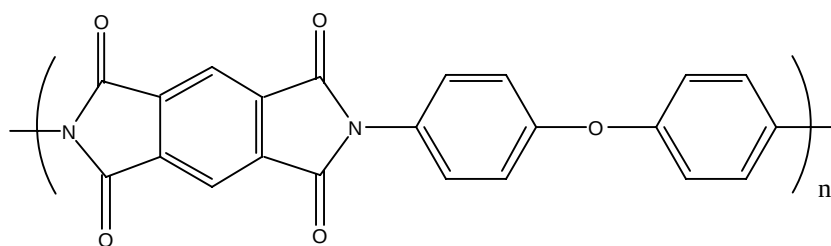


Figure 2.2.1.2.1 The Repeat Unit of Kapton-H Formed from PMDA and ODA¹⁹

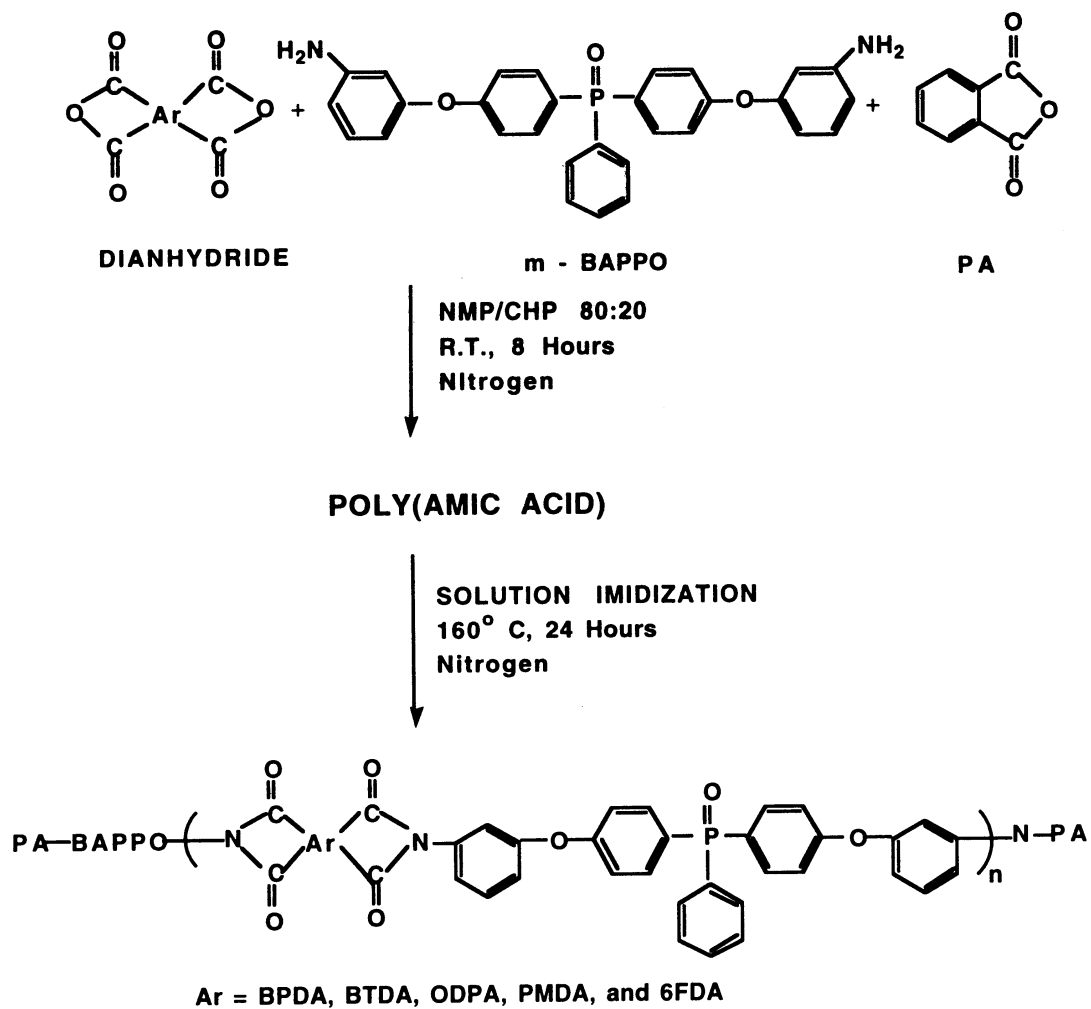
is required to fully cyclize the PAA. Chain mobility can also be achieved above the glass transition temperature of the polyimide.

2.2.1.3 Solution Imidization

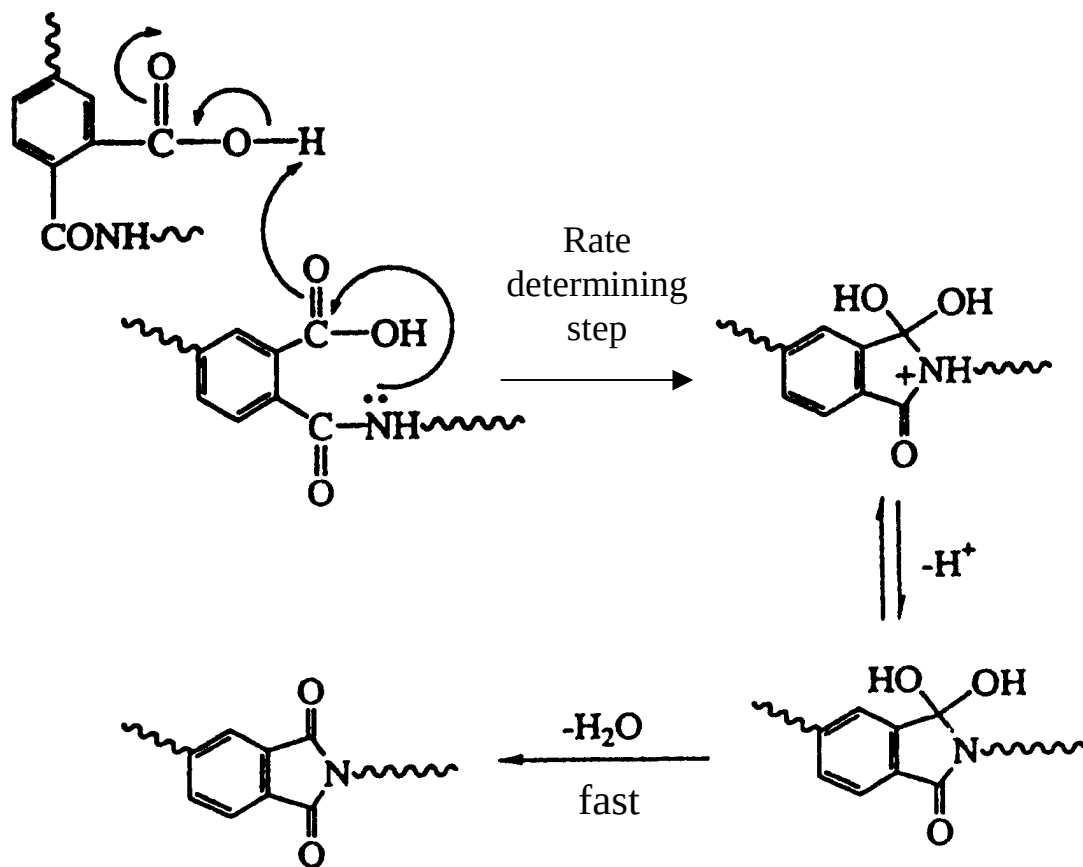
Polyimides which remain soluble in the fully cyclized form can be thermally imidized from the corresponding PAA's in solution at elevated temperatures. A typical solvent combination and temperature profile is shown in Scheme 2.2.1.3.1.²⁰ An azeotroping solvent is typically used in order to remove the water formed during the reaction to drive the reaction to completion. The solvent of choice needs to be capable of transporting the water from the reaction. Typical azeotroping solvents are: toluene, xylene, o-dichlorobenzene (o-DCB), or cyclohexyl pyrrolidone (CHP).

Kim et al. has recently proposed a reaction mechanism for the imidization of homogeneous systems in solution (Scheme 2.2.1.3.2).²¹ The rate determining step in this process, which was recently confirmed by Furukawa et al.,²² is second order with respect to PAA links and is also acid catalyzed. Imidization was also monitored by titration analysis as a function of temperature (Figure 2.2.1.3.1).²¹ Initially, the viscosity of the PAA solution was high but as the reaction temperature increased, a dramatic decrease in the solution viscosity was observed. The drop in viscosity has also been noted by others during solution imidization.²³⁻²⁵ The initial drop in viscosity could be interpreted as resulting from the following: a shift in the equilibrium from the PAA back to the free amine/anhydride and/or an acid-catalyzed hydrolysis of amide bonds.²¹ In either case, the chain undergoes scission, which has been confirmed by ¹H NMR measurements. The subsequent viscosity build up is due to the restoration of long chains as scissioned units reunite and subsequently cyclodehydrate to form the high molecular weight polyimide.

Complete backbone cyclization, shown in Figure 2.2.1.3.1, occurred at 180°C within 12 hours. However, even after 24 hours at lower temperatures, eg. 140°C and 150°C, incomplete imidization was evident. It is well known that incomplete imidization will affect the end use properties because the residual amide linkages are readily



Scheme 2.2.1.3.1 Synthesis of m-BAPPO Based Polyimides via Solution Imidization²⁰



Scheme 2.2.1.3.2 A Reaction Mechanism for the Solution Imidization Process²¹

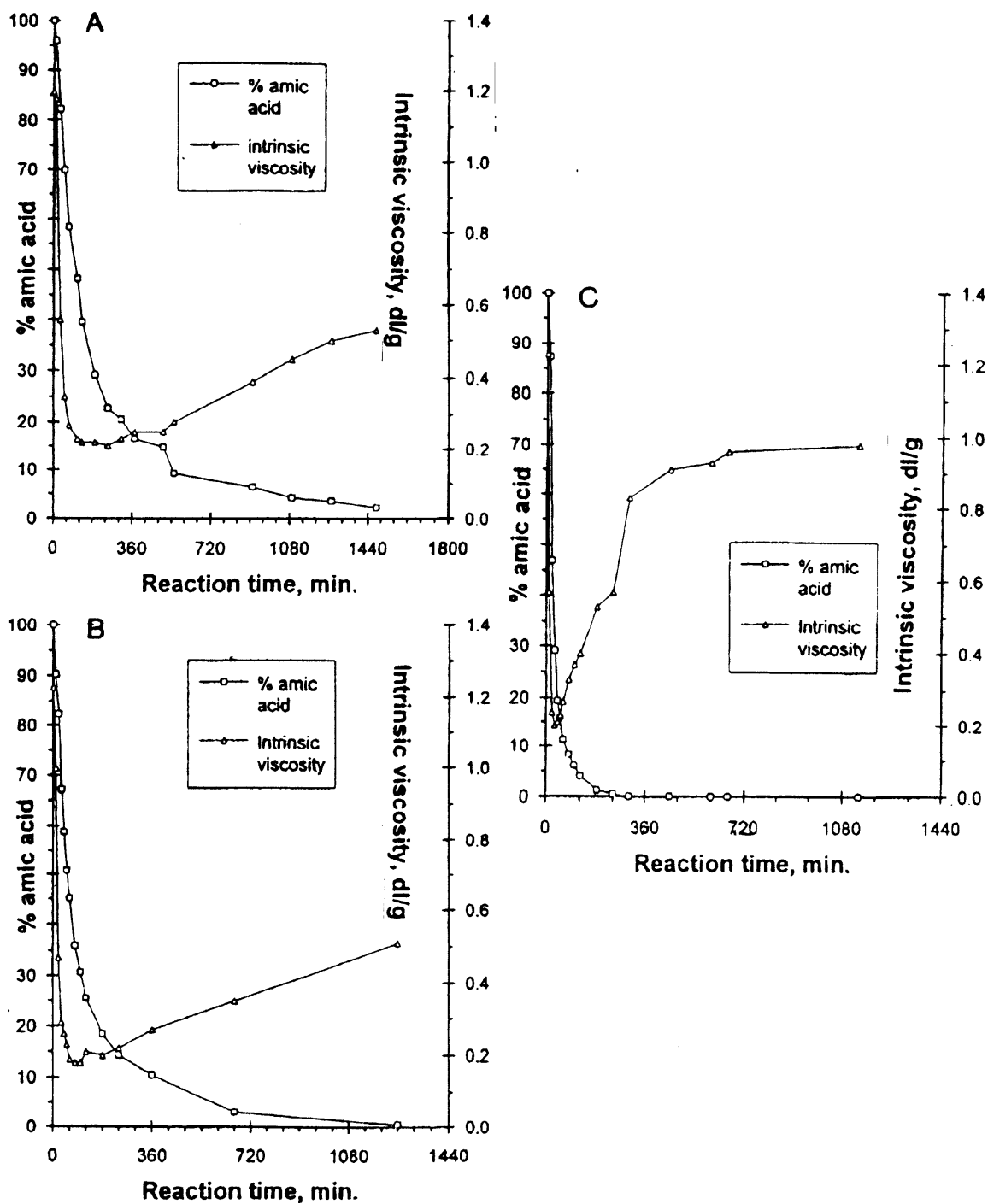


Figure 2.2.1.3.1 Remaining Amic Acid Content and Intrinsic Viscosity as a Function of Reaction Time: (A) at 140°C; (B) at 150°C; (C) at 180°C²¹

hydrolyzed due to the ortho-carboxyl group which promotes nucleophilic attack of water, leading to chain scission.¹

2.2.1.4 Chemical Imidization

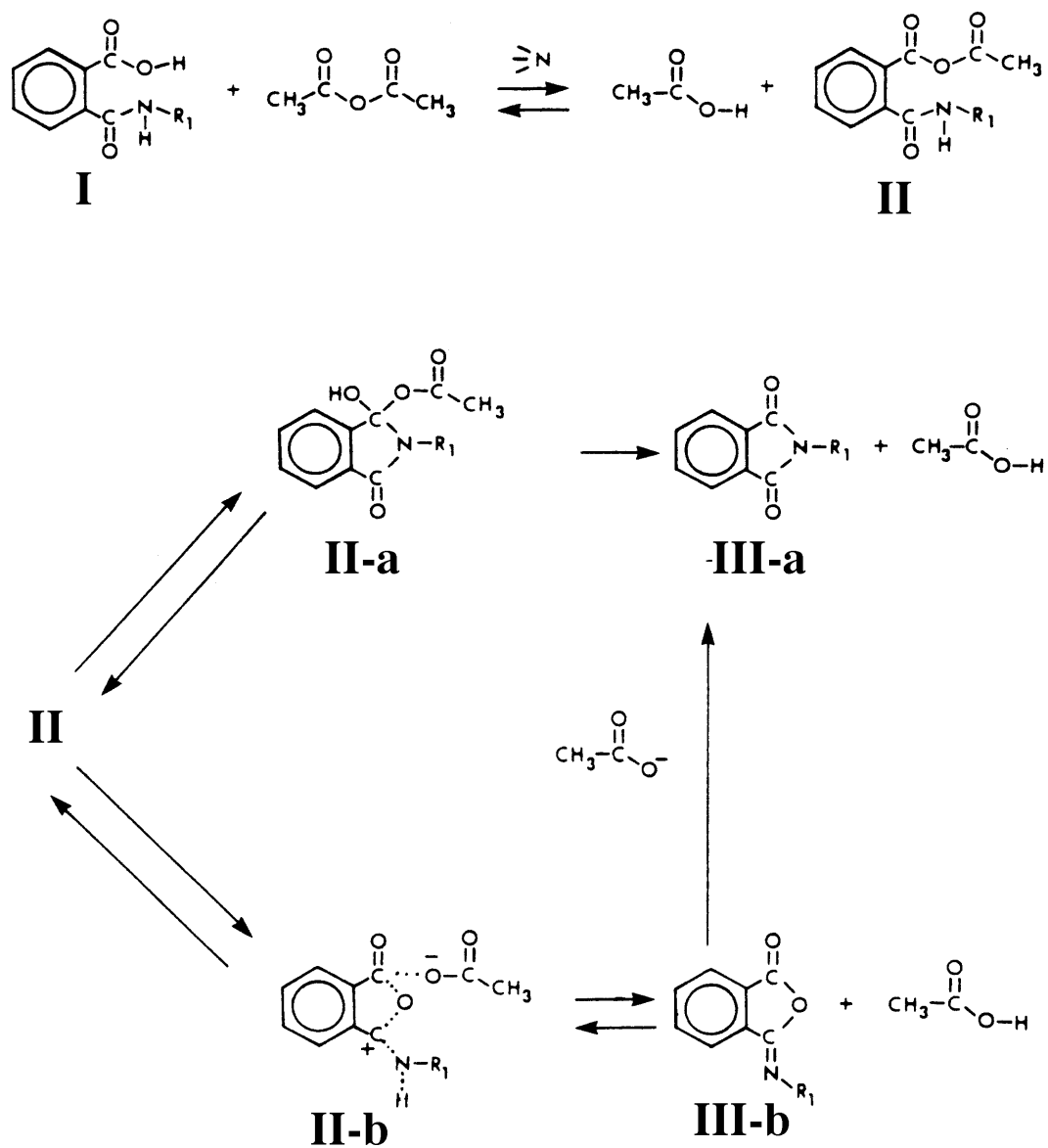
Cyclodehydration of PAAs can be accomplished at room temperature or slightly higher with chemical reagents (Scheme 2.2.1.4.1).^{19,26,27} Various combinations of chemical reagents have been used to affect this conversion. The preferred product of the reaction, either a polyimide (III-a) or a polyisoimide (III-b), will be determined by the selection of chemical reagent. Dehydrating agents such as anhydrides of carbonic, formic and acetic acids can be used in conjunction with a tertiary amine such as pyridine, 2-methylpyridine, triethylamine, and isoquinoline, to bring about the polyimide formation. The mechanism of formation involves a mixed anhydride intermediate followed by an iminolactone and then the imide linkage, which is the thermodynamically favored product (Scheme 2.2.1.4.1-III-a).²⁸

Alternatively, PAAs can also be converted to the polyisoimide with a number of other chemical reagents (Scheme 2.2.1.4.1-III-b).²⁹⁻³² A combination of pyridine and trifluoroacetic anhydride favor isoimide formation.³¹ The polyisoimides can be thermally converted to the polyimide or they can serve as reactive intermediates.³³ Post-reactions of polyisoimides with amines, alcohols, thiols or hydrazoic acid result in poly(amide-imide), poly(amide-ester), poly(amide-thioester) and polytetrazole acid, respectively.

Landis prepared a number of polyisoimide oligomers with thermally curable endgroups.^{34,35} He found that polyisoimides are more soluble than their related polyimide structure. In fact, the most significant feature of polyisoimides is improved solubility/processability over that of polyimides.

2.2.2 Additional Routes to Polyimides

2.2.2.1 Polyimides From Dianhydrides and Diisocyanates



Scheme 2.2.1.4.1 Chemical Imidization and Isoimidization of Poly(amic acid)s³²

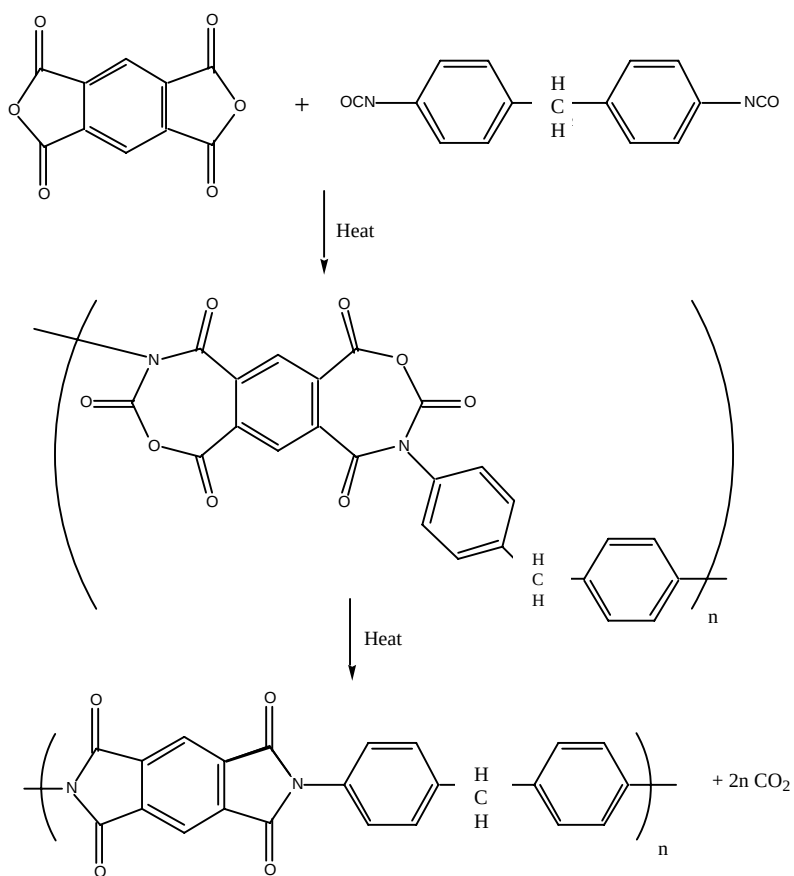
Dianhydrides and diisocyanates can react to form polyimides with elimination of carbon dioxide as a byproduct. Although the mechanism has not been fully elucidated, it has been proposed that it proceeds through an imide-anhydride seven-membered ring at 40°C (Scheme 2.2.2.1.1).³⁶ Upon further heating, carbon dioxide is liberated and the polyimide is formed. Many of the earlier polymers prepared using this route were found to have low molecular weight and to be insoluble. More recently, the catalyst induced formation of polyimides in dipolar solvents using alkali metal alkoxides and phenoxide yielded high molecular weight polymers.^{37,38} Kakimoto et al. has recently reported obtaining soluble polyimides in benzonitrile using bulky diisocyanates (Scheme 2.2.2.1.2).³⁹

The potential for side reactions is one of the drawbacks in using this preparation method. For example, isocyanates can undergo dimerization, cyclotrimerization, and even polymerization to form nylon-1.⁴⁰

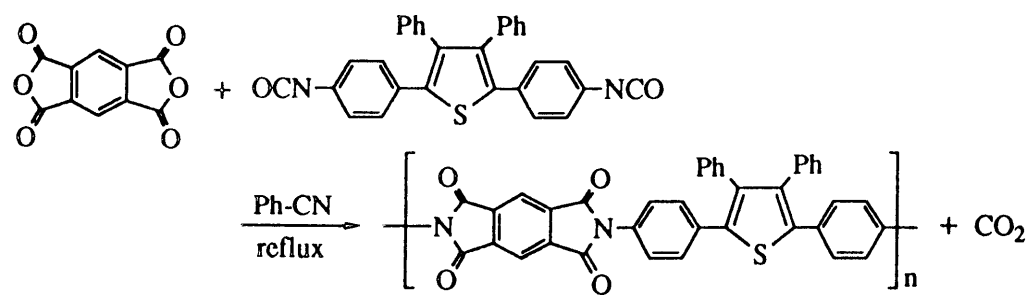
2.2.2.2 Nucleophilic Aromatic Substitution

Nucleophilic aromatic substitution reactions are well known synthetic methods for preparing poly(arylene ether-ketone)s and poly(arylene ethersulfone)s and may be used to form ether or sulfide linked polyimides (commercially available Ultem could be produced using this route).⁴¹ To form the polyimides, a strongly activated bis-aromatic halo-^{42,43} or nitro-⁴⁴⁻⁴⁶ monomer containing precyclized imide moieties was reacted in a dipolar aprotic solvent with either a bisphenol or bithiol salt (Scheme 2.2.2.2.1).⁴⁷ The intermediate encountered, enroute to the final product, is the Meisenheimer complex, which is effectively stabilized through resonance by the imide system (Scheme 2.2.2.2.2).⁴⁸

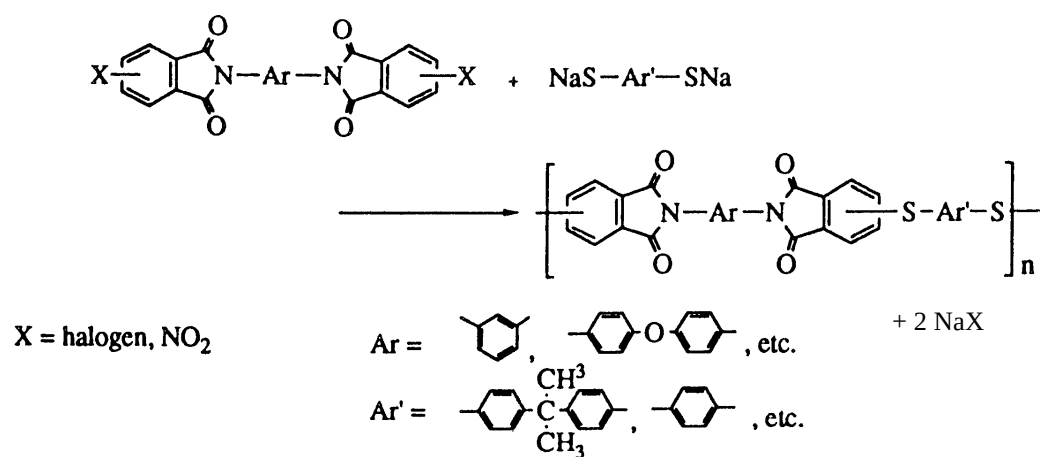
Recently, Kricheldorf et al.^{49,50} modified this procedure for polyarylene ethers to bypass the use of oxygen-sensitive anhydrous bisphenol salts and to eliminate the need for removal of the salt by-product from the reaction (Scheme 2.2.2.2.3). Others have employed this methodology using an A-B type monomer to form polyimides (Figure 2.2.2.2.1).⁵¹



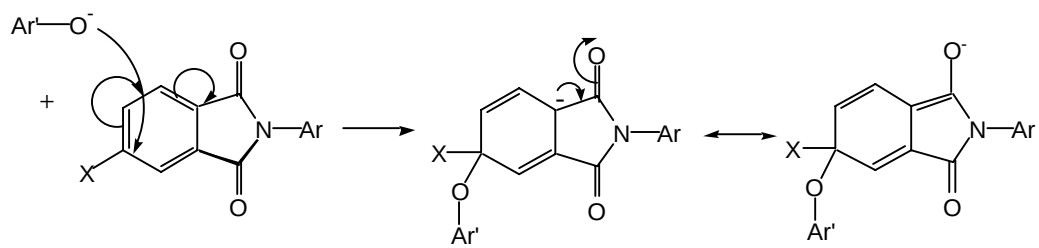
Scheme 2.2.2.1.1 Proposed Route to Polyimides from Dianhydrides and Diisocyanates via an Imide-Anhydride Seven-Membered Ring³⁶



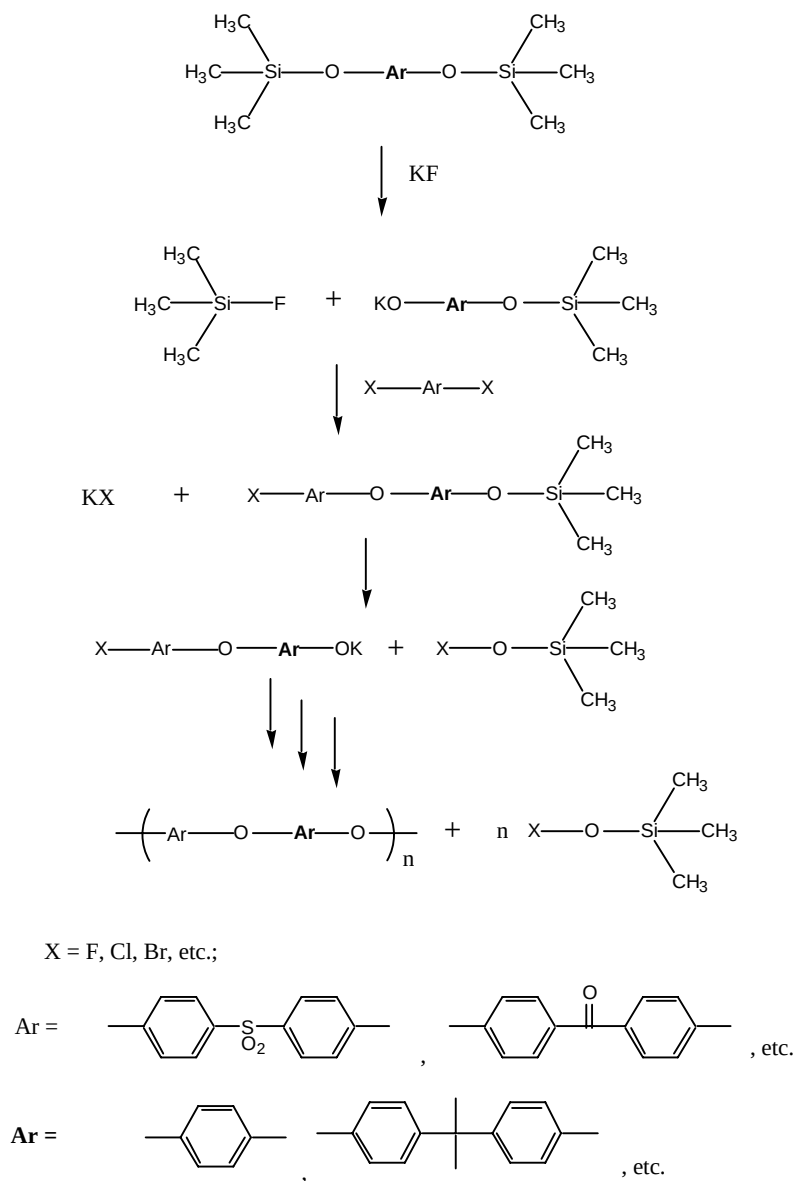
Scheme 2.2.2.1.2 Preparation of a Polyimide from a Dianhydride and a Diisocyanate with Bulky Substituents³⁹



Scheme 2.2.2.2.1 Synthesis of Polythioetherimides by Aromatic Nucleophilic Substitution⁴⁷



Scheme 2.2.2.2.2 The Meisenheimer Transition State⁴⁸



Scheme 2.2.2.2.3 Synthesis of Polyarylene Ethers from Bis(trialkylsilyl)ethers of Bisphenols and Activated Bishalo Compounds^{49,50}

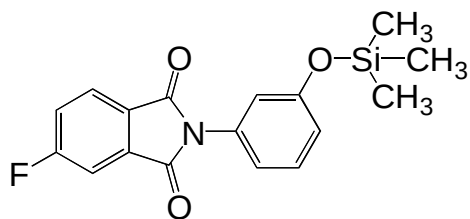


Figure 2.2.2.2.1 A-B Type Monomer to Form Polyimides⁵¹

2.2.2.3 Ester-Acid Route

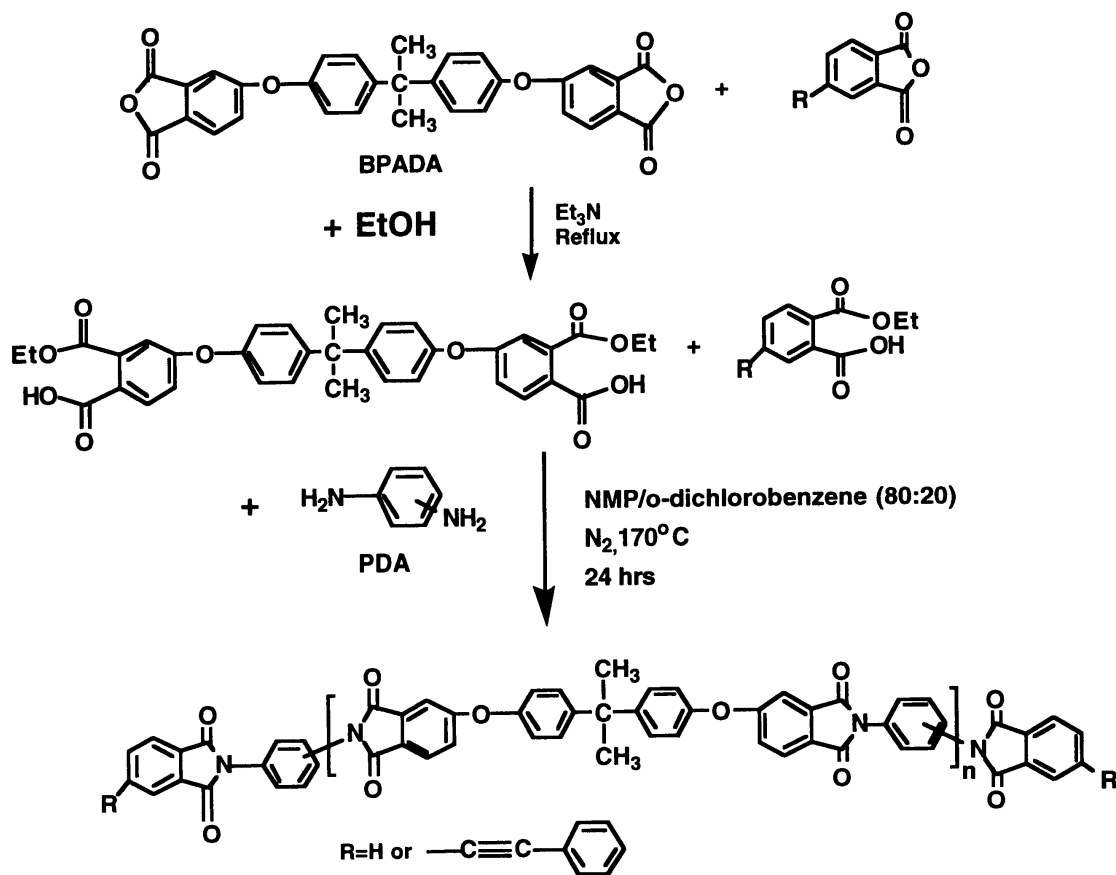
The ester-acid precursor method for polyimides can be employed with aromatic diamines in solution.⁵² In this synthetic route, the monomeric dianhydride is pre-reacted with an alcohol such as methanol or ethanol to form the o-ester-acid of the dianhydride (Scheme 2.2.2.3.1).⁵² This reaction can be catalyzed by a tertiary amine such as triethylamine. Huang et al. recently reported on the ring opening selectivity of various dianhydrides toward alcohols (Figure 2.2.2.3.1).⁵³ The isomeric ratios of diester-diacids were found to be independent of alcohol structure but quantitatively correlated with the electron affinities of the different bridging groups (Scheme 2.2.2.3.2 & Table 2.2.2.3.1).⁵³

The resulting isomeric diester-diacids are much more soluble and are possibly less toxic than the corresponding dianhydrides. Additionally, they are relatively stable towards moisture. Essentially, the ester-acid acts as a protecting group for the otherwise hydrolytically unstable anhydride. A commercial example typically synthesized by the ester-acid route is the thermosetting PMR-15 resin (Polymers from Monomeric Reagents, $M_n \sim 1,500$ g/mole) (Scheme 2.2.2.3.3).⁵⁴

It has been shown that at higher temperatures (100-150°C) the anhydride functionality is reformed from the ester-acid.⁵⁵ The work of Moy et al. proved that nucleophilic attack on the ester carbonyl by the diamine did not occur.⁵⁵ Instead the ester-acid reverts to the anhydride at elevated temperatures (eg. >140°C) thereby becoming reactive toward amines. Consequently, the rapid formation of amic acid ensues, followed by cyclodehydration to form polyimide at these high temperatures. This process has the advantage of being a ‘one-pot’ reaction.⁵⁶

2.2.2.4 Transimidization

High molecular weight homo- or co-polyimides can also be prepared via a transimidization reaction involving an amine-imide exchange with either aromatic or aliphatic diamines, or aminopropyl functional siloxane oligomers (Scheme 2.2.2.4.1).⁵⁷⁻⁶⁰ The driving force for the bis(etherimide)-diamine exchange is the production of a less



Scheme 2.2.2.3.1 Synthesis of Phthalic Anhydride and/or Phenylethynyl Phthalic Anhydride Endcapped Polyimides via the Ester-Acid Route⁵²

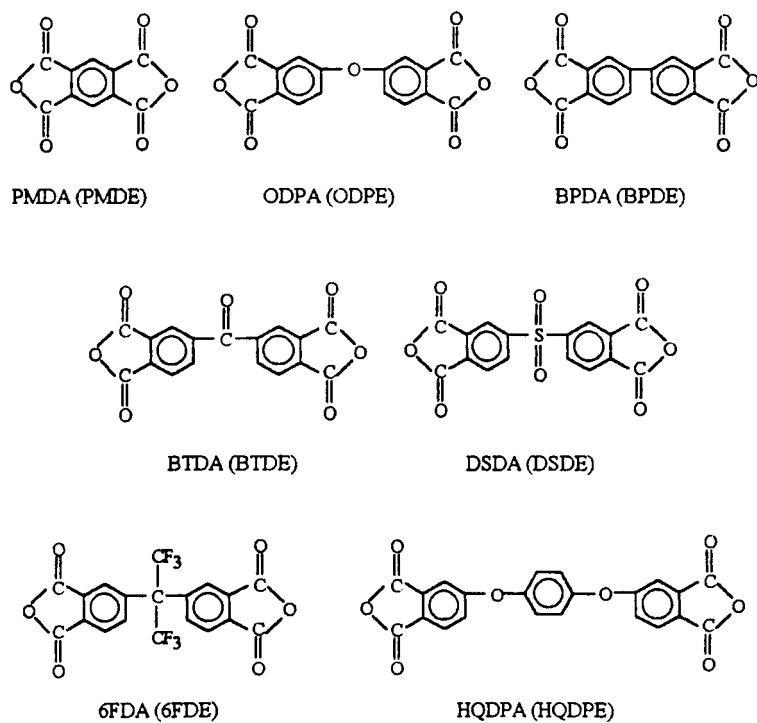
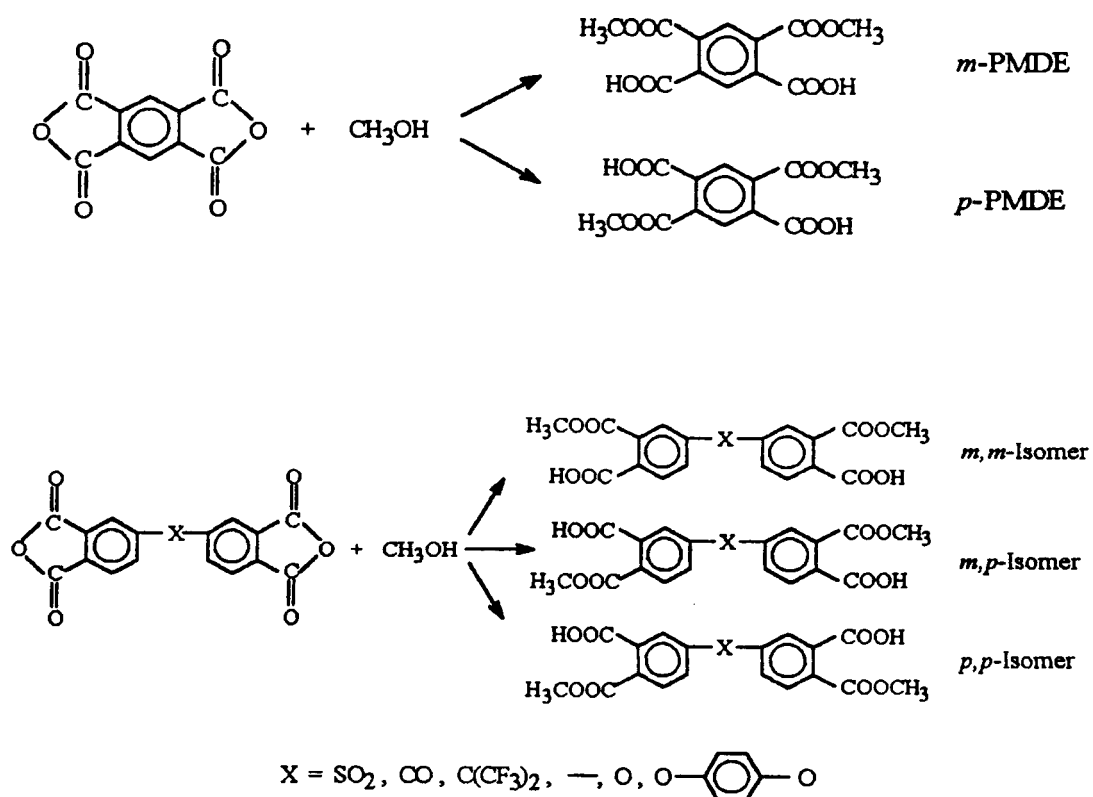


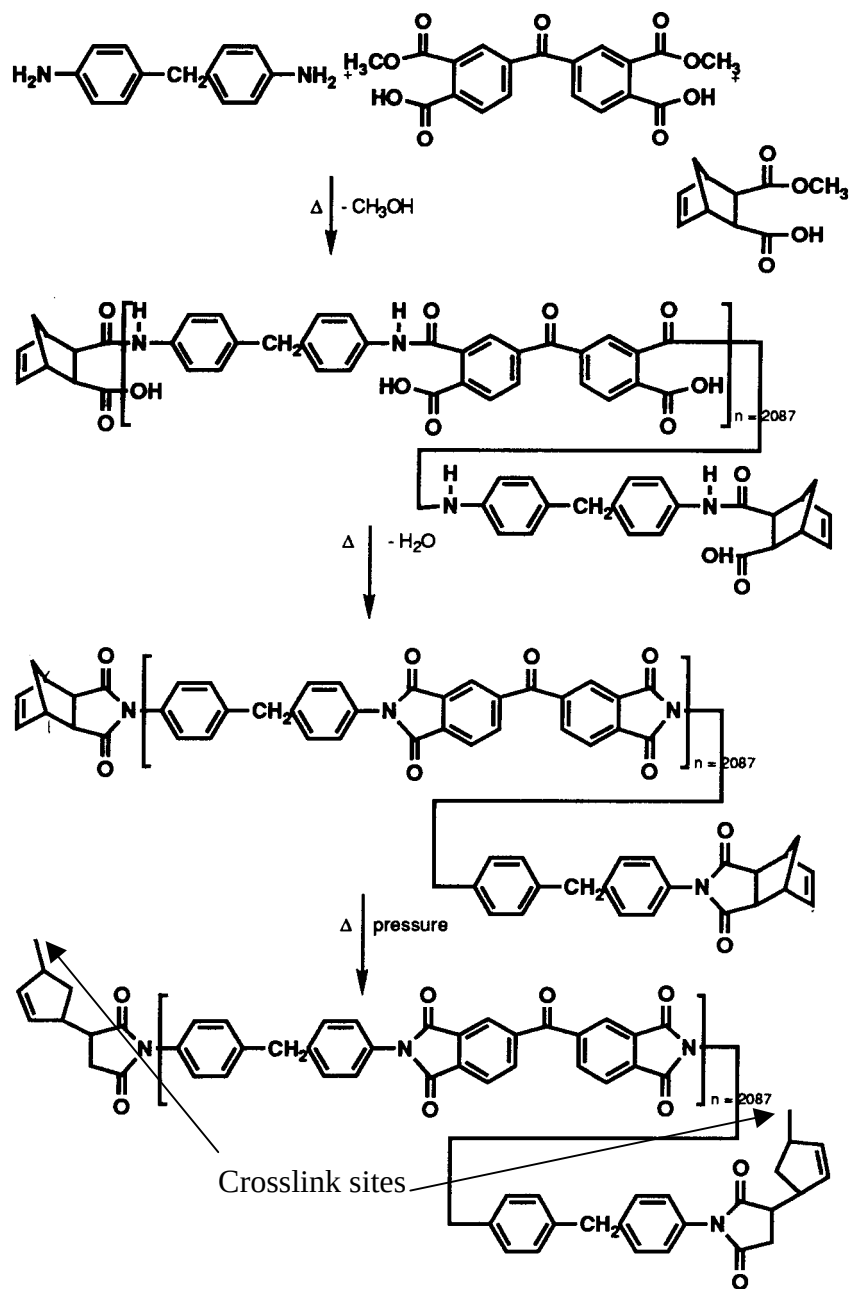
Figure 2.2.2.3.1 Dianhydrides for Methanolysis Reactions⁵³



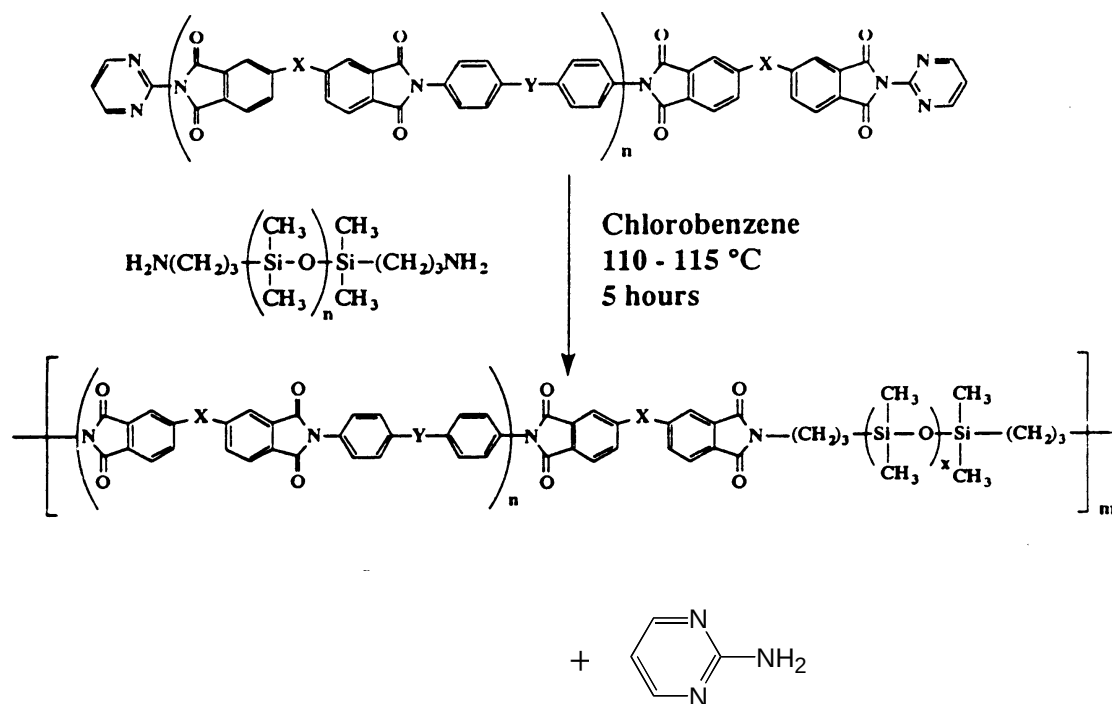
Scheme 2.2.2.3.2 Synthesis of the Three Isomers of Diester-Diacids Prepared from Bridged Dianhydrides⁵³

Diester-diacids	EA ⁺	Relative abundance	
		<i>Para</i>	<i>Meta</i>
DSDE	1.57	0.62	0.38
BTDE	1.55	0.57	0.43
6FDE	—	0.52	0.48
BPDE	1.38	0.43	0.57
ODPE	1.30	0.34	0.66
HQDPE	1.19	0.26	0.74

Table 2.2.2.3.1 E_a (eV) and Relative Abundance of *meta*- and *para*-positions⁵³



Scheme 2.2.2.3.3 PMR-15 Resin Chemistry Utilizing the Ester-Acid Route⁵⁴



Scheme 2.2.2.4.1 Synthesis of Perfectly Alternating Segmented Imide Siloxane Copolymers⁶⁰

basic byproduct. To obtain high molecular weight polymer, the difference in basicities must be large or the diamine byproduct must be removed during the reaction. It has been found that even though the reaction equilibrium favors the starting material when a more basic amine is the byproduct, a number of catalysts, such as carboxylate salts of zinc, lead, and cadmium, can be used to form high molecular weight polyimides.⁶¹ Webb et al.⁶² and Takekoshi et al.⁵⁸ demonstrated that 2-amino pyridine is readily exchanged by common aromatic diamines.

2.2.2.5 Other Routes to Polyimide Formation

Many other polyimide preparation methods have been reported in addition to the aforementioned routes. Due to the improved stability and solubility of derivatized PAAs, a number of techniques have been developed to form alkyl esters,⁶³⁻⁶⁷ silyl esters,^{68,69} and ammonium salts^{70,71} of PAAs, all of which can be thermally cyclized to form polyimides. The alkyl esters are formed from the reaction of an ester-acid chloride and the silylated esters are formed in the reaction of N,N'-bis(trialkylsilyl) diamines with various dianhydrides. The ammonium salts of PAA's can be formed by reaction with a secondary or tertiary amine. The resulting polyelectrolyte can then be dispersed in an aqueous medium and used to fabricate carbon fiber composites.⁷¹

Polyimides can also be prepared by Diels-Alder⁷²⁻⁷⁵ and Michael^{76,77} cycloaddition reactions. Palladium catalyzed carbon-carbon coupling reactions have also been reported in the literature^{78,79} as well as methods utilizing a 'one-step' process which bypasses the PAA precursor.^{80,81}

2.3 Polyimide Properties and Applications

2.3.1 Characterization and Properties of Polyimides

2.3.1.1 *Molecular Weight and Functional Group Analysis via Titration Measurements*

Precise control of molecular weight, molecular weight distribution, and reactive groups is an important goal of polymer science. Left undetermined these parameters can significantly effect polymer properties. For example, while polymers may have identical repeat units and number average molecular weights, their polydispersities may be different. Polymers with different polydispersities can greatly influence thermal and mechanical properties.^{82,83} In addition, specific functional groups are known to influence polymer crystallization⁸⁴ and lead to crosslinking side reactions.⁸⁵ In order to probe these important polymer parameters, exact techniques for measuring these parameters are needed.

Molecular weight determination is of primary importance in polymer science due to the number of inherent properties this parameter reflects. Solubility is required for determining polymer molecular weight by solution techniques. Unfortunately, many polyimides are insoluble due to crystallinity, chain rigidity or network formation. Although many polyimides are insoluble, their precursor polyamic acids (PAAs) are soluble. However, hydrolytic instability of the o-carboxylic amide linkage requires that careful procedures need to be followed to correctly assess molecular weight. Soluble polyimides can be fully characterized more easily.

Solution viscosity is perhaps the easiest method to investigate viscosity average molecular weight. It is a very useful technique, especially if the empirical Mark-Houwink constants have been determined. However, the molecular weight distribution cannot be assessed and it is necessary to utilize additional techniques to better define the system.

The technique most widely used for investigating molecular weight is gel permeation chromatography (GPC), which is also known as size exclusion chromatography (SEC). When properly calibrated, GPC allows the determination of the number-, viscosity-, weight- and 'z'- average molecular weights. Moreover, the polymer-

solvent pair constants, K and a , and the radius of gyration, R_g , can also be determined. Grubisic et al.⁸⁶ showed that polymers with the same hydrodynamic volume elute from a column at the same volume, regardless of chemical nature and architecture. The product of intrinsic viscosity and molecular weight is used to define this parameter, which has been termed Universal Calibration.

It is common to use a series of nearly monodisperse polystyrene samples of varying molar mass to generate a calibration curve for GPC. Thus, it is common to report molecular weights relative to those of polystyrene standards. However, in many cases the actual molecular weight value can be quite different. This problem can be eliminated if the GPC is coupled to a viscosity detector allowing the absolute molecular weight to be determined via the universal calibration procedure.

Konas et al.^{87,88} found that good mobile phases for polyimides were among the following: chloroform, tetrahydrofuran, N-methylpyrrolidone (NMP) with 0.06M LiBr, or NMP stirred over P_2O_5 before use. The addition of lithium bromide and P_2O_5 eliminated spurious high molecular weight peaks, which suggests that they suppress specific polyelectrolyte or other similar effects.⁸⁷

Functional group analysis via titration experiments is a complimentary technique to GPC. Titration experiments may be conducted to determine the concentration of a particular reactive group in the polymer. It can also reveal the extent of imidization by determining the percent residual carboxylic acid groups. Titration also enables measurement of the number average molecular weight of polymers based on reactive endgroups. To establish a well-defined polyimide system, endgroup titration results, as well as spectroscopic endgroup analysis, can be correlated with the molecular weight data obtained from GPC.

Other important techniques used to determine polymer molecular weight include membrane osmometry (for M_n),⁸⁹ light scattering (for M_w),^{89,90} and low angle laser light scattering (LALLS) (for M_w).^{91,92}

2.3.1.2 Structural Characterization

A number of structural changes occur during polyamic acid formation and subsequent imidization. Several methods, including Fourier transform infrared (FTIR), Raman and UV spectroscopies, as well as ^1H , ^{13}C , ^{15}N and ^{19}F NMR spectroscopies have been used to understand these chemical transformations.⁹⁶

Functional groups are conveniently measured using FTIR. Characteristic absorptions are observed for the imide, anhydride, amine, isoimide and amic acid moieties. Table 2.3.1.2.1 lists the absorption bands for each of these structures.⁹³⁻⁹⁵ Although a great deal of structural information can be found in the later stages of imidization, FTIR cannot detect small amounts of uncyclized amic acid groups due to low sensitivity. However, FTIR can give semiquantitative data on the imidization process.⁹⁶

NMR spectroscopy may also be used to monitor the imidization process. Imide conversion can be monitored from the ^1H NMR signal intensities of COOH protons. In one system, imidization was initiated at 70°C and was completed at 200°C.⁹⁷ ^{13}C NMR spectroscopy has been utilized to monitor thermal and chemical imidization as well as depolymerization.⁹⁸ ^{19}F NMR has also been conducted on fluorine-containing polyimides and the results were found to correlate with carbon-fluorine coupling constants.⁹⁹

2.3.1.3 *Glass Transition Temperature and Thermal Stability*

The glass transition temperature (T_g) is the temperature at which a polymer undergoes extensive cooperative segmental motion along the backbone. The T_g may also be described as the relaxation point which occurs between the glassy and rubbery plateaus. A number of intra- and intermolecular interactions may affect the T_g , including electrostatic and ionic interactions, hydrogen bonding, chain packing efficiency and chain stiffness. In particular, the chain stiffness has been found to affect the T_g to a great extent.

Differential scanning calorimetry (DSC), among other analytical methods, is routinely utilized to probe the T_g of polymers by monitoring the heat capacity as a function of temperature. The T_g is a second order endothermic transition.

Table 2.3.1.2.1 Infrared Absorption Bands of Imides and Related Compounds⁹³⁻⁹⁵

	Absorption band (cm⁻¹)	Intensity	Origin
Aromatic imides	1780	s	C=O asym. Stretch
	1720	vs	C=O sym. Stretch
	1380	s	C-N stretch
	725		C=O bending
Isoimides	1795-1820	s	Iminolactone
	1700	m	Iminolactone
	921-934	vs	Iminolactone
Amic acids	2900-3200	m	COOH and NH(2)
	1710	s	C=O (COOH)
	1660 amide I	s	C=O (CONH)
	1550 amide II	m	C-NH
Anhydrides	1820	m	C=O
	1780	s	C=O
	720	s	C=O
Amines	3200 two bands	w	NH(2) sym. Structure (v(s)) NH(2) asym. Structure (v(as)) $v(s) = 345.53 + 0.876 \cdot v(as)$

vs, very strong; s, strong; m, medium; w, weak

Table 2.3.1.3.1 shows the T_g s of four BTDA based polymers that differ in diamine structure.¹⁰² The T_g increases with chain stiffness which is a function of the diamine bridging unit in the BTDA series. The methylene-bridged diamine allows a greater degree of bond rotation about the linking group, leading to the lowest T_g . Similarly, the flexible ether-linked diamine lowers T_g . However, by changing the bridging group to a carbonyl, the T_g increases, due to an increase in chain rigidity. Chain rigidity is a function of the reduced rotation about the $-(O)C$ -aryl single bond, which has more double bond-like character. The sulfone linkage has strong electron withdrawing capabilities, which causes the T_g to continue increasing, even though the out-of-plane, bulky SO_2 functionality could potentially hinder chain packing. Again, the higher T_g for this system could be related to more double bond like character between the bridging and aryl groups.

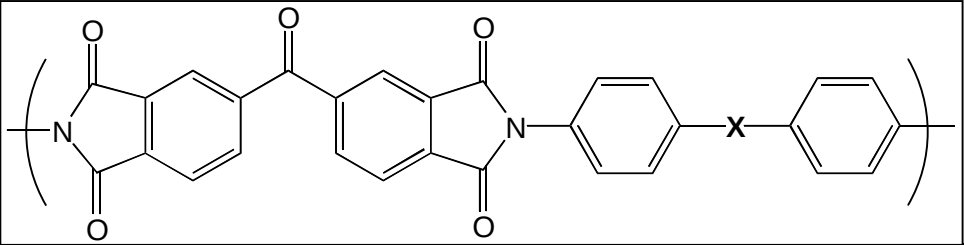
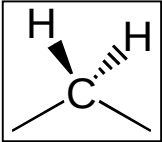
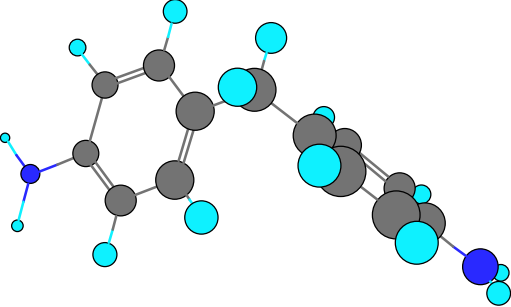
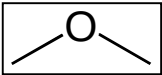
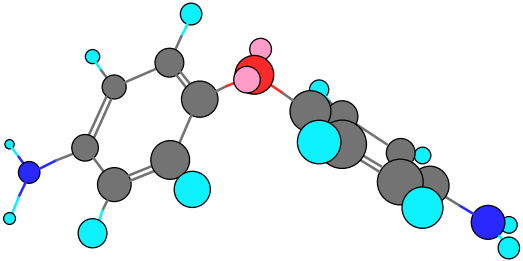
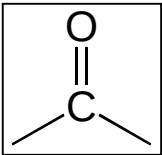
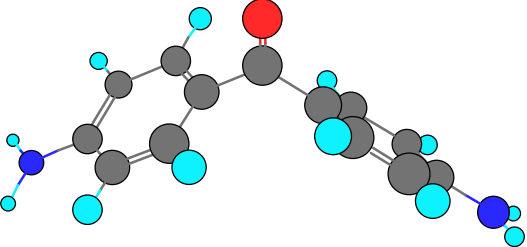
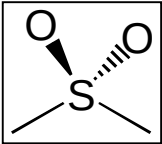
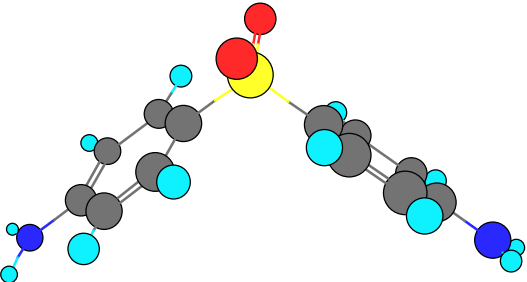
Bell et al.¹⁰³ has reported the influence of diamine catenation on T_g . From Table 2.3.1.3.2, it is clearly illustrated that *ortho* and *para* linked systems lead to higher T_g s when compared to their *meta* linked counterparts. The presence of *ortho* and *para* linked benzophenone diamine moieties can give rise to a strong dipolar unit,¹⁰³ thereby decreasing chain flexibility.

The thermal stability of polymers is often analyzed by thermogravimetric analysis (TGA) either under air or nitrogen. TGA monitors polymer weight loss as a function of temperature either under dynamic or isothermal conditions. Under dynamic conditions (10°C/min) the 5% weight loss value is often over 500°C for wholly aromatic polyimides. Chemical moieties that decrease the thermal stability of polyimides may be aliphatic or benzylic protons; hydroxyl groups and other less thermally stable functionalities.

2.3.1.4 Insolubility/Infusibility

Insolubility and infusibility of some polyimides has been attributed to crosslinks formed during the imidization process. Although this is undoubtedly true in some cases, there are other possible causes such as charge transfer complexes¹⁰⁰ and semi-crystallinity.¹⁰¹ For the PMDA/ODA polyimides, crosslinking cannot be the sole

Table 2.3.1.3.1 The Effect of Bridging Unit on the Glass Transition Temperature (T_g)¹⁰²

		
Diamine Bridge (X)	Diamine 3-D Rendering	T_g
		234*
		236
		255
		273

*Cured to 300 deg. C in vacuum

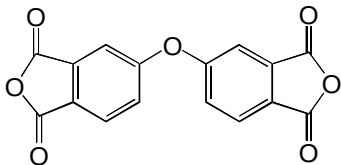
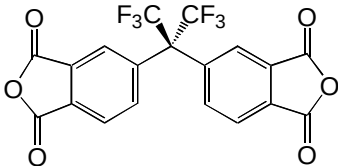
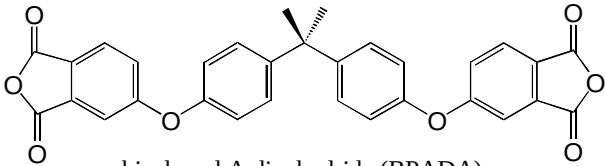
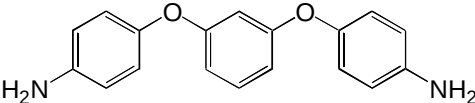
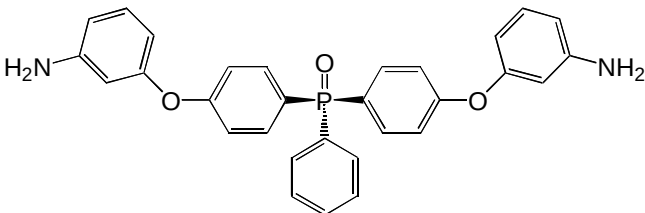
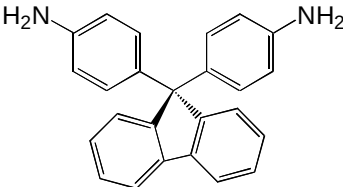
contributor to insolubility because although these systems are insoluble in common organic solvents, they are fully soluble in concentrated sulfuric acid.

Often, insolubility is due to very rigid macromolecular chains. Improvement in polymer solubility has been accomplished in at least four ways.¹⁰²

1. Polar groups have been placed either pendant to or along the backbone
2. Bulky groups have been employed as either pendant or bridging groups
3. Chain flexibility has been promoted by *ortho* and *meta* catenation versus *para* catenation
4. Chain flexibility has been promoted by linking groups with greater rotational freedom, such as, -O-, -CH₂-, -SO₂-, -(CH₃)₂- and -C(CF₃)₂-.

Table 2.3.1.4.1 presents some monomers that may increase solubility when incorporated into polyimides based on their chemical structural features.

Table 2.3.1.4.1 Common Dianhydrides and Diamines with Various Structural Features

Dianhydride/Diamine	Category
 4,4'-oxydiphthalic anhydride (ODPA)	1,4
 hexafluoroisopropylidene dianhydride (6FDA)	2,4
 bisphenol A dianhydride (BPADA)	1,4
 1,3-bis(4-aminophenoxy)benzene (TPER)	1,3,4
 bis-(3-aminophenoxy-4'-phenyl) Phenylphosphine Oxide (m-BAPPO)	1,2,3,4
 9,9-bis(4-aminophenyl) Fluorene (FDA)	2

2.3.2 Polyimide Applications

2.3.2.1 Polyimides in Electronics

Polymers are widely used in the electronics field in areas such as wafer fabrication, adhesion, chip packaging and assembly.¹⁰⁴⁻¹¹¹ Polyimides have found a great deal of utility in wafer fabrication as photoresists due to their excellent performance at elevated temperatures, corrosion resistance and their ability to be spin-coated onto substrates. They also serve as insulators, which prevent “cross-talk” between conducting vias, and as adhesives between polymer-polymer and polymer-metal interfaces. Polyimides may also be designed so that their coefficient of thermal expansion (CTE) more closely matches that of the supporting substrate, which is generally a metal (Figure 2.3.2.1.1).¹¹² By matching the CTE of the metal, the polyimide-metal interface experiences very little stress associated with thermal cycling, which otherwise may cause premature failure.

Photosensitive polyimides are used in electrical devices where a submicron pattern is needed to route electrical current. They also eliminated the complex multistep processing used in the high-resolution photolithography process needed for nonphotosensitive materials. The properties of a photosensitive polyimide are changed upon exposure to light. The exposed portion of the polyimide undergoes crosslinking or scission chemical changes that either inhibit or promote solubility, respectively. If light exposure inhibits solubility, the polymer is said to be negatively-imaged.^{113,114} However, if light exposure promotes solubility the resin is said to respond positively.¹¹⁵

A typical negative-imaging photosensitive polyimide is shown in Figure 2.3.2.1.2.¹¹⁵ Upon exposure to light, the derivatized polyamic acid undergoes crosslinking which renders it insoluble. The unexposed region, which is still relatively soluble, can be removed by solvent development. The final curing step causes the cleavage and volatilization of the crosslink while simultaneously forming the heterocyclic imide structure. A negative-image response can also be promoted through polyimide in-chain functionalities which are photo-excitable. The most widely known polyimide of this

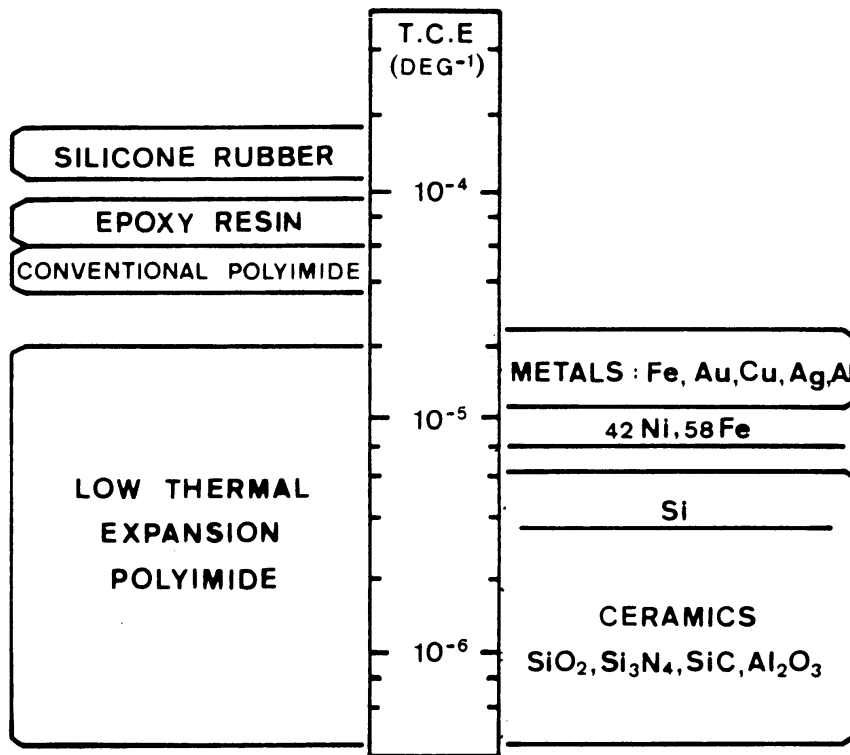


Figure 2.3.2.1.1 The Coefficient of Thermal Expansion of Various Metals, Ceramics and Organic Polymers¹¹²

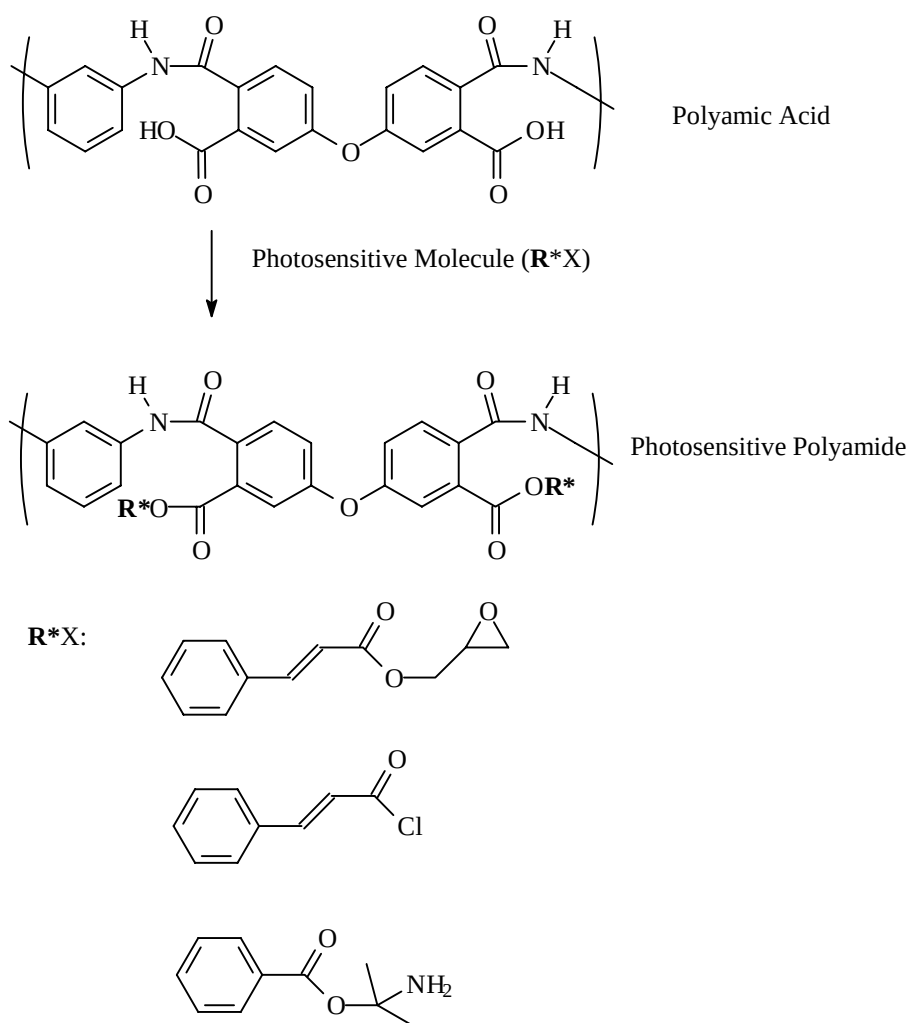


Figure 2.3.2.1.2 Typical Negative-Imaging Photosensitive Polyimide¹¹⁵

type contains a photosensitive benzophenone carbonyl and labile benzylic or methylene protons, which can be abstracted by the excited carbonyl moiety. An interchain bond is formed when two carbon radicals combine to form a carbon-carbon bond. These materials have the advantage of being fully cyclized before exposure, which allows the shrinkage upon curing to be greatly reduced.

Positive photoresist polyimides¹¹⁶⁻¹¹⁹ become more soluble when exposed to the correct wavelength of light. An increase in solubility is observed when the backbone undergoes cleavage or when the polarity of side groups changes. Ho et al.¹¹⁷ recently reported silylating hydroxyl groups in a polyimide backbone. The trimethoxysilane bond was found to undergo hydrolysis in the presence of a photoacid-generating molecule. The solubility differential between the silylated and non-silylated polyimide allowed them to be selectively developed.

2.3.2.2 Polyimides as Optical Waveguides

The function of an optoelectronic device is to convert electrical signals to optical signals, transport the signals through space, and reconvert them to electrical signals. Optical waveguides are reflective channels which allow information in the form of light to be transported through a medium by internal reflection.¹²⁰ Optical waveguides have the advantage of being able to transport multiple signals simultaneously without affecting each other while having both immunity to electromagnetic interference, and noninteraction when signals cross.¹²¹ The prevailing method for telecommunication relies heavily on optoelectronic devices.

Both freestanding and embedded waveguides are well known.¹²¹ The former consist of a polymeric material coated onto a substrate that is patterned by photolithography, laser ablation, or ion beam etching techniques. The pattern allows the transmission of light through the remaining polymer structure. Embedded waveguides use UV lithography to record a pattern onto a polymeric material by altering its chemical structure, thereby facilitating selective diffusion. Selective ion-diffusion of dye molecules can change the refractive index of the material.

The process requirements for waveguide materials exceed those found in many thermoplastics. A typical flip-chip configuration, in which the active chip area faces the substrate, is shown in Figure 2.3.2.2.1.¹²² Materials used in this configuration need to withstand chip joining temperatures of up to 360°C, must be patternable to fit between C4 connections, need to allow signal detection by transmitting the information through the beveled plane reflector, and must not be influenced by organic solvents. Polyimides, which are well known for their excellent thermal stability, good dimensional stability, and high decomposition temperatures, can satisfy these material requirements.¹²¹

Polyimides that are thermally imidized from the polyamic acid were found to show large optical losses, which is inappropriate for the waveguide application. Upon polyamic acid cyclization to the polyimide and solvent removal, it was found that microvoids formed causing density fluctuations and light scattering leading to an optical loss in the material. On the other hand, fully imidized polyimides show a significant reduction in optical loss. By incorporation of bulky side groups, such as 6F and 3F, the polyimide can be used in the fully cyclized form.¹²³ The 6F and 3F groups also promote solubility, hinder chain ordering and chain transfer complexes, and give high T_g materials, all of which are favorable for this application.¹²¹

2.3.2.3 Polyimides in Aerospace

A number of structurally modified polyimides have been developed to meet the increasing demands of our societies' growing technology. The aerospace industry is one of those areas in which the material demands are ever increasing. Researchers have met this challenge primarily with polyimides, which can be modified to meet processing conditions while maintaining several of their advantageous properties.

Polyimides¹²⁴⁻¹²⁸ are known to have excellent heat and chemical resistance, excellent adhesion to a number of substrates, and superior mechanical properties, such as high flexural modulus and compressive strength. Polyimides are also known to possess outstanding dimensional stability under loads, which allows their use in high temperature environments. The addition of phosphorus substituents is known to impart fire-retardancy as evidenced by high TGA char yields in air. Lee et al.¹²⁷ found that the

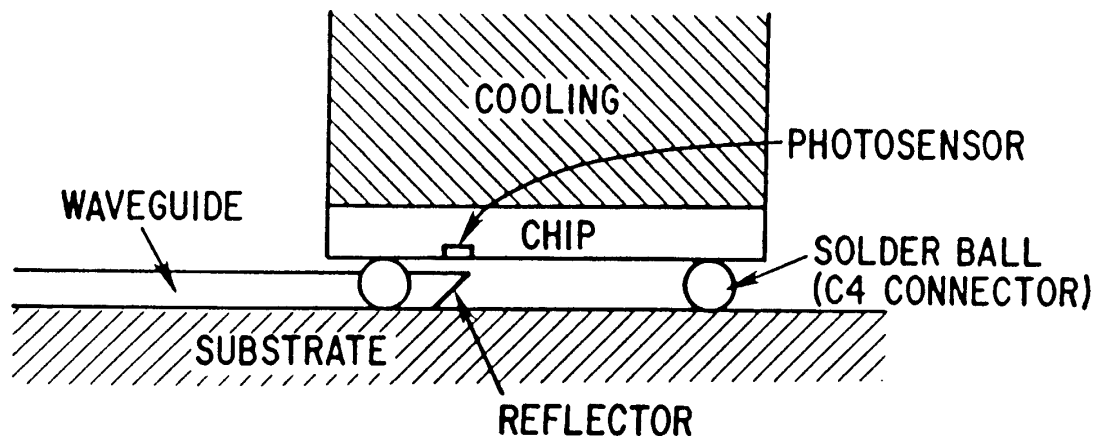


Figure 2.3.2.2.1 Flip-Chip Configuration with Waveguide¹²²

incorporation of bis(*m*-amino phenoxy)triphenylphosphine oxide not only improved fire-retardancy but also solubility and adhesive strength to titanium.

The performance of polyimide composites surpasses that of mechanically fastened assemblies in terms of fatigue and corrosion resistance, aerodynamic properties, manufacturing costs, and repairs.¹²⁴ Due to these outstanding properties and economical advantages, polyimides are used in the aerospace industry as struts, brackets, composites, and structural adhesives.¹²⁴⁻¹²⁸

Composite applications, such as those found in aerospace, require the resin material to thoroughly wet the matrix, such as carbon fibers. In order to promote good wettability, the polyimide can be introduced as an oligomer. Oligomers, capped with reactive endgroups, exhibit lower melt viscosities and can undergo crosslinking at elevated temperatures. Commercial examples of these systems are shown in Table 2.3.2.3.1.¹²⁸ PMR-15 contains low molecular weight oligomers end-capped with nadic anhydride which undergo crosslinking at 250°C-300°C. The drawbacks of the PMR-15 is the volume of solvent removed such as methanol, water and cyclopentadiene, which produces voids in the final laminate. High temperature, void free systems can be achieved with acetylene, phenylacetylene, and phenylethynyl terminated oligomers.^{52,129-131,157}

2.3.2.4 *Polyimide Adhesives in Aerospace and Microelectronics*

Defining specific chemical interactions which lead to an adhesive bond has proven to be quite complex due to the number of variables involved. Several researchers have developed theories to explain and predict this type of interaction. The generally accepted theories of adhesion¹³²⁻¹³⁴ are:

1. Mechanical Interlocking (or hooking): the adhesion is due to tortuous path of fracture

Table 2.3.2.3.1 Curable Polyimides for Aerospace Applications^{128, 302}

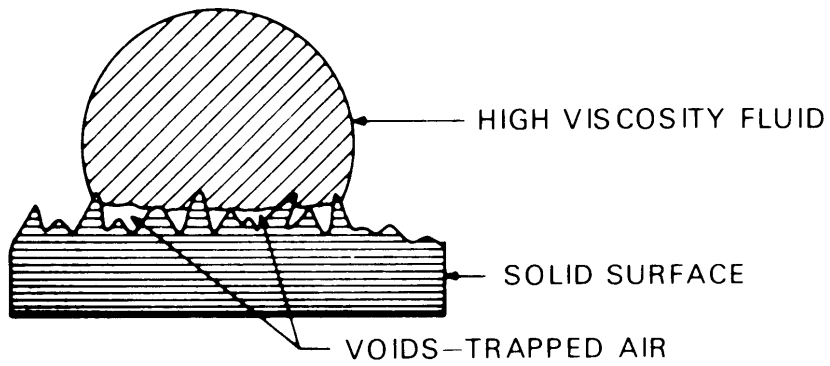
Monomers	Unsaturated end cap	Examples
methylenedianiline, benzophenone dianhydride	nadic imide	PMR-15 LARC-13
methylenedianiline, maleic anhydride	maleimide	Kerimid 601
methylenedianiline, benzophenone dianhydride	phenylacetylene	ATPI Thermid
m-phenylene, bisphenol A dianhydride	phenylethynyl ^{52,157}	

2. Surface Energetics: good wetting is required for good adhesion (Figure 2.3.2.4.1)¹³⁵
3. Diffusion Theory: interpenetrating network formation occurs across the interface to form an interphase region
4. Acid-Base Theory: strength of the acid-base interaction affects adhesion strength
5. Chemical bonding: physical bond formation leads to adhesive strength
6. Weak Boundary Layer Mechanism: invoked to explain poor adhesion relating to cohesive failure in the interfacial region

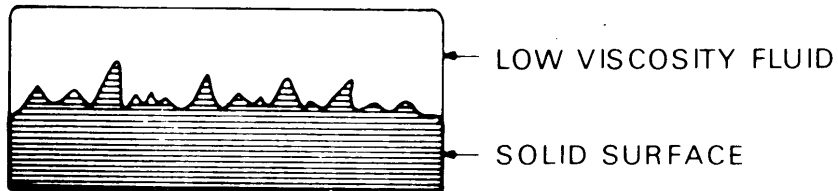
It is impossible to explain adhesion by any one of these mechanisms, although one mode of adhesion may be predominant and lead to the majority of the observed adhesive strength.^{136,137} The most desired interaction at the polymer/substrate interface is often proposed to be a chemical bond.^{138,139} Unlike Van der Waals forces and hydrogen bonding, chemical bonds are much less likely to be disturbed by heat, water and exposure to chemicals.

Surface contaminants will play a significant role in chemical interactions and bond durability and complicate the matter of adhesion,. Figure 2.3.2.4.2¹³⁵ depicts a typical surface with a number of adsorbed contaminants. It is essential to properly prepare the surface prior to polymer application. This can be done in a number of ways ranging from a pumice scrubber and heat treatments to reactive ion etching and chemical modification.¹⁴⁰

Polyimide adhesives fall into one of three classes based on their adhesion characteristics.^{141,142} The first class is amorphous polyimides, which self-adhere and bond well with metals such as Cu, Cr and Al. Semicrystalline polyimides form the second class of polyimide adherents. This class, in general, adheres well to reactive metals such as Al and Cr, but not to unreactive metals like Cu. Presumably, this is due to hindered



LOW AREA OF INTERFACIAL CONTACT RESULTING FROM
HIGH VISCOSITY OF FLUID



LACK OF VOIDS AND HIGH AREA OF INTERFACIAL CONTACT
RESULTING FROM LOW VISCOSITY OF FLUID

Figure 2.3.2.4.1 Effect of Adhesion Viscosity on Interfacial Contact¹³⁵

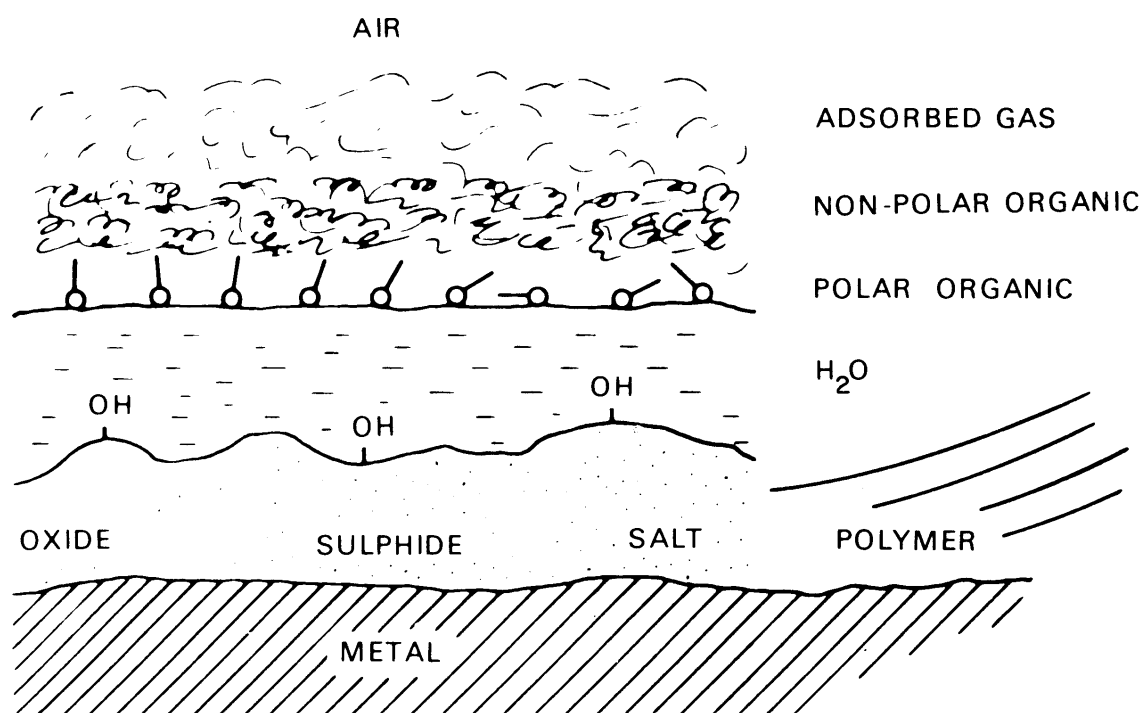


Figure 2.3.2.4.2 Hierarchy of Spontaneously Adsorbed Layers on a Metal Surface¹³⁵

molecular mobility within the more ordered regions. Some semicrystalline polyimides also exhibit marginal self-adhesion. Brown et al.¹⁴³ showed that polyimide/polyimide adhesion is influenced by the cure temperature before adhesive bond formation. The bond strength between two fully cured (400°C) polyimides (ODA/PMDA) was weak whereas the bond strength between one fully cured polyimide with an incompletely cured polyimide (200°C) was good. The interdiffusion region between each set of polymer films was higher for the fully cured/incompletely cured laminent than it was for the fully cured/fully cured laminent (47nm vs. 30nm).¹⁴³

Thermosetting resins represent a third class of polyimide adherents. Low molecular weight polyimides with curable endgroups allow for good wetting and adhere well to metals, ceramics and to themselves, if one of the layers remains uncured prior to adhesive bond formation.¹⁴²

A number of geometries and test configurations can be used to determine material adhesive strength (Figure 2.3.2.4.3).¹³² The adhesive strength values determined by each method in Figure 2.3.2.4.3 will vary with each methodology due to stress distributions in loaded adhesive joints generally being non-uniform.¹³²

A structural adhesive is a bonding agent used for transferring required loads between adherents exposed to service environments typical for the structure involved.¹⁴⁴ Structural adhesives in aerospace applications need to withstand a number of extreme and dynamic environments ranging from radiation bombardment to reduced pressure (10^{-6} - 10^{-17} torr) and thermal cycling (-160°C to 120°C or -256°F to 248°F).¹⁴⁵⁻¹⁵⁰ A missile in flight must be able to withstand a temperature of 500°C (932°F) for a few minutes and on aircraft for the high speed civil transport project must withstand temperatures ranging from 177°C to 232°C (351-450°F) for more than 50,000 hours. Truly, polymeric materials that satisfy these rigorous requirements qualify as “space-age” polymers.

Polyimides are leading candidates for aerospace applications⁴ due to their excellent thermooxidative stability, good adhesion to metals and good mechanical properties over a wide range of temperatures. PMR-type chemistry (polymerization of monomeric reactants), which employs nadic anhydride endgroups, is a leading resin for this application (Scheme 2.3.2.4.1).¹⁵¹ A potential drawback to using this material is the

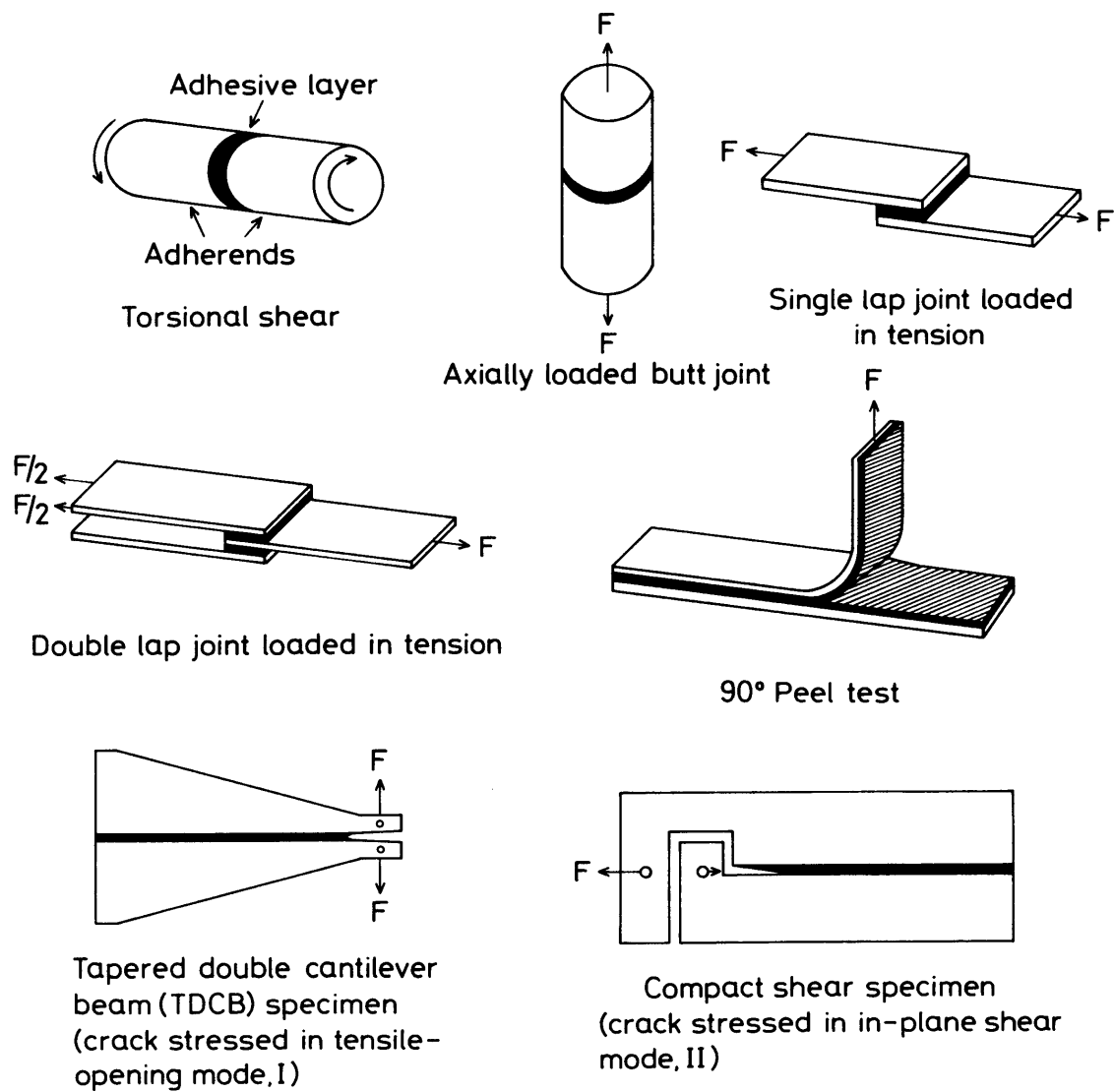
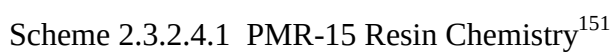


Figure 2.3.2.4.3 Sketches of Adhesive Joint Geometries¹³²



evolution of cyclopentadiene upon thermal crosslinking. Evolution of volatiles may produce a significant number of voids in the bondline,¹³⁵ which will reduce long-term adhesion.

The family of polyimide oligomers terminated with acetylene,^{131,152-154} phenylacetylene¹⁵⁶⁻¹⁵⁸, phenylmaleimide^{129,159} or phenylethynyl^{52,157} reactive endcaps are alternatives to PMR-type chemistry. These materials, which may be fully cyclized, do not emit volatiles when thermally crosslinked at elevated temperatures and exhibit good adhesion to metals. They also have excellent shelflife, low crosslink density, excellent solvent resistance when cured, and wide processing windows between the glass transition temperature and cure exotherm (Figures 2.3.2.4.4 and 2.3.2.4.5).¹⁵⁸

Microelectronic devices such as printed circuit boards and multichip packages also rely on good adhesion between polyimide-polyimide and polyimide-metal interfaces. For this application, polyimide precursors, either the polyamic acid (PAA) or polyamic ester (PAE), are generally applied to the desired substrate from solution to form a thin polymer layer, which can be imidized at elevated temperatures. This process involves a number of chemical and physical changes, many of which have not been sufficiently addressed due to the complexity of adhesive behavior.

Imidization of the PAA or PAE thin film results in loss of water, residual solvent and other volatile components present in the film. Because of the loss of volatiles and differences in the thermal coefficient of expansion between the film and substrate, the film experiences residual stress build-up.^{161,162} Residual stress may lead to premature adhesive failure. The surrounding environment, such as humidity and temperature, in which the device operates will also affect the stress build-up¹⁶³ and bond stability.¹⁶⁴ Polyimides are known to absorb various amounts of water from their surroundings which may disrupt adhesion. This is illustrated by the common laboratory practice of applying water to remove polyimide films from glass substrates. Interfacial adhesion characteristics may be improved with coupling agents such as aminosilanes and aluminum chelates¹⁶⁵ (Figure 2.3.2.4.6).¹⁶⁶

Ozawa and coworkers¹⁶⁷ reported data on a series of fully cyclized Probimide® photoimageable polyimides and compared them with PAA precursors of Kapton. These

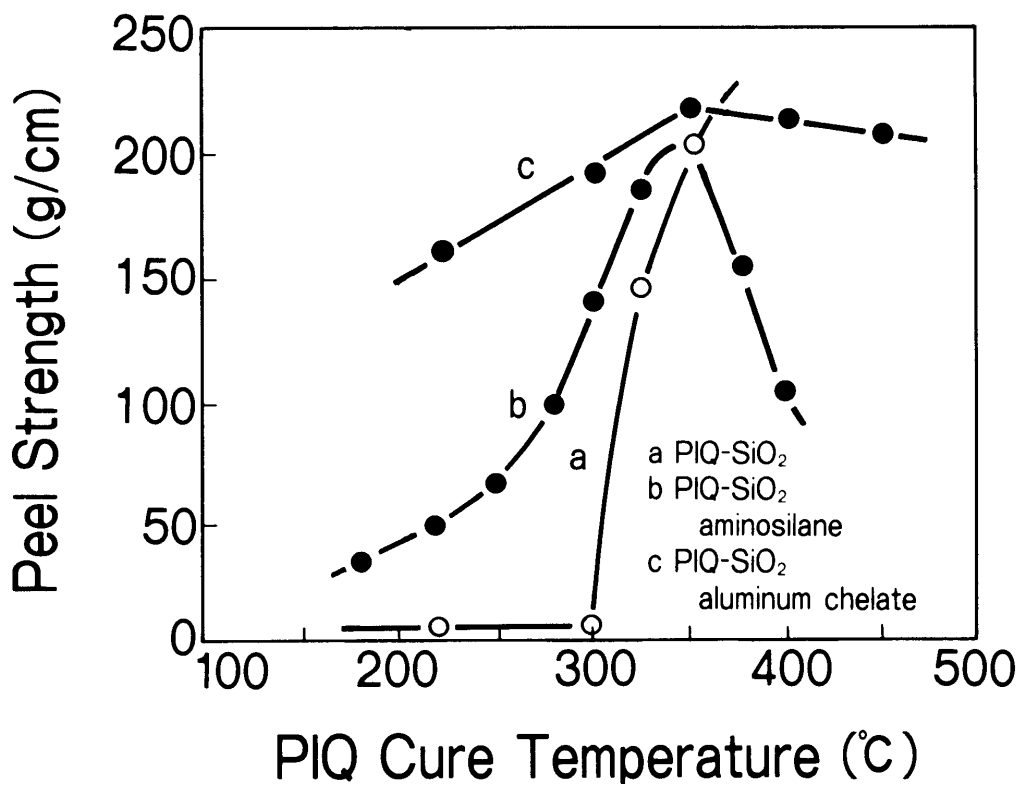
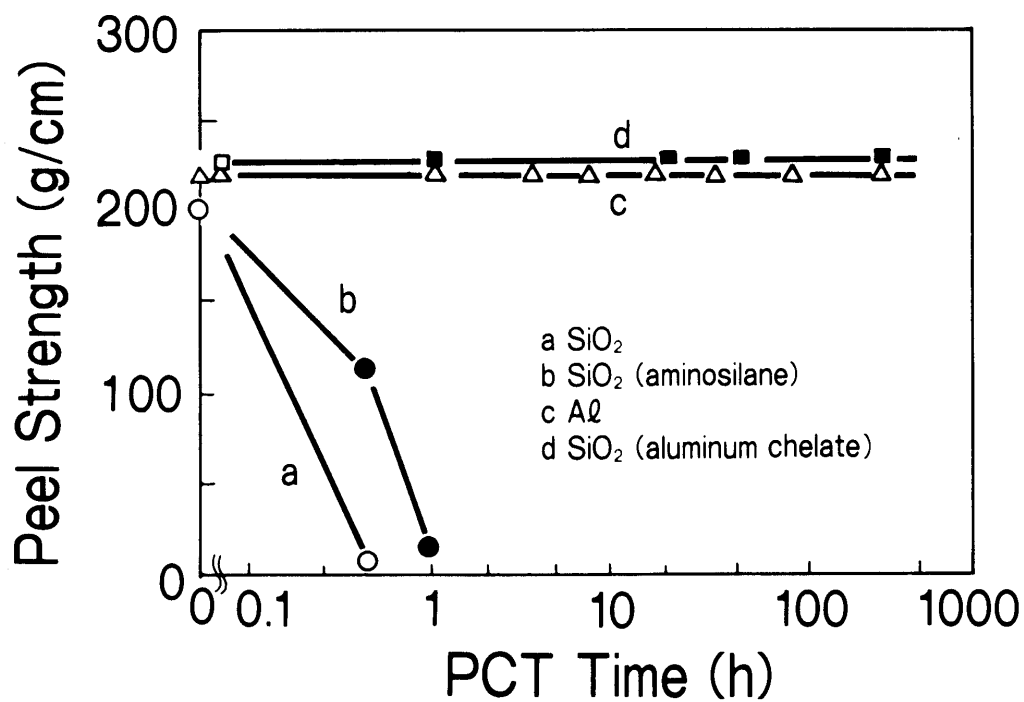


Figure 2.3.2.4.6 Adhesion Properties of PolyimideIsoindoloquinazolinedione (PIQ) to SiO₂ with and without Adhesion Promoter (aminosilane)¹⁶⁶

authors applied a typical cure schedule used in photolithography to each polymer, namely, 30 minutes at 110°C (soft bake) followed by 2-14 hours at 350°C (hard bake). Shrinkage of the polyamic acid materials ranged from 30-60% due to cyclization, which produces water, and residual solvent removal. The refractive index of the PAAs also changes dramatically upon conversion to the polyimide. On the other hand, the cyclized Probimide® series showed minimal shrinkage as well as constant refractive indices. Polymers, which maintain constant refractive indices and UV spectra over a wide range baking conditions, are useful for fabricating multilayered structures such as multichip modules.¹⁶⁵

2.4 Gas Transport in Polymeric Membranes

This section will address the theory and physical description fundamental to the two methods for separating gas molecules. A brief description of gaseous diffusion through a porous membrane will be followed by an analogous treatment of dense films, including gas transport properties above and below T_g . The former is presented to illustrate the need for efficient and economic methods for separating gases.

2.4.1 Porous Membranes

Gas flow in porous membranes may be considered to be a competition between Knudsen flow and Poiseuille flow (Figure 2.4.1.1). Knudsen flow is favored if the membrane pore radius (r) is less than the mean free path of the penetrant (λ). Poiseuille flow exists when there are more collisions with other gas molecules than with the pore walls (e.g. a concentrated solution). If Poiseuille flow dominates, each of the gas molecules is coupled with another. Therefore, in the case of a bicomponent gas mixture, there will be no effective separation. The literature shows that poiseuille flow is predominant (>90%) when the ratio r/λ is greater than about 5.¹⁶⁸

Porous membranes must operate in the Knudsen flow regime because when there is little or no separation of gas molecules occurring under Poiseuille flow conditions. When Knudsen flow governs the mode of separation, gas molecules are momentarily absorbed and then reflected in a random direction, resulting in few encounters with other gas molecules. Accordingly, the mean free path term is dominant. The mean free path is defined as

$$\lambda = (3\eta/2P) * (\pi RT/2M)^{1/2} \quad \text{Equation 1}$$

where M =gas molecular weight, P =pressure, η =viscosity of the gas, R =the universal gas constant, and T =temperature. As the gas molecules traverse the separating medium

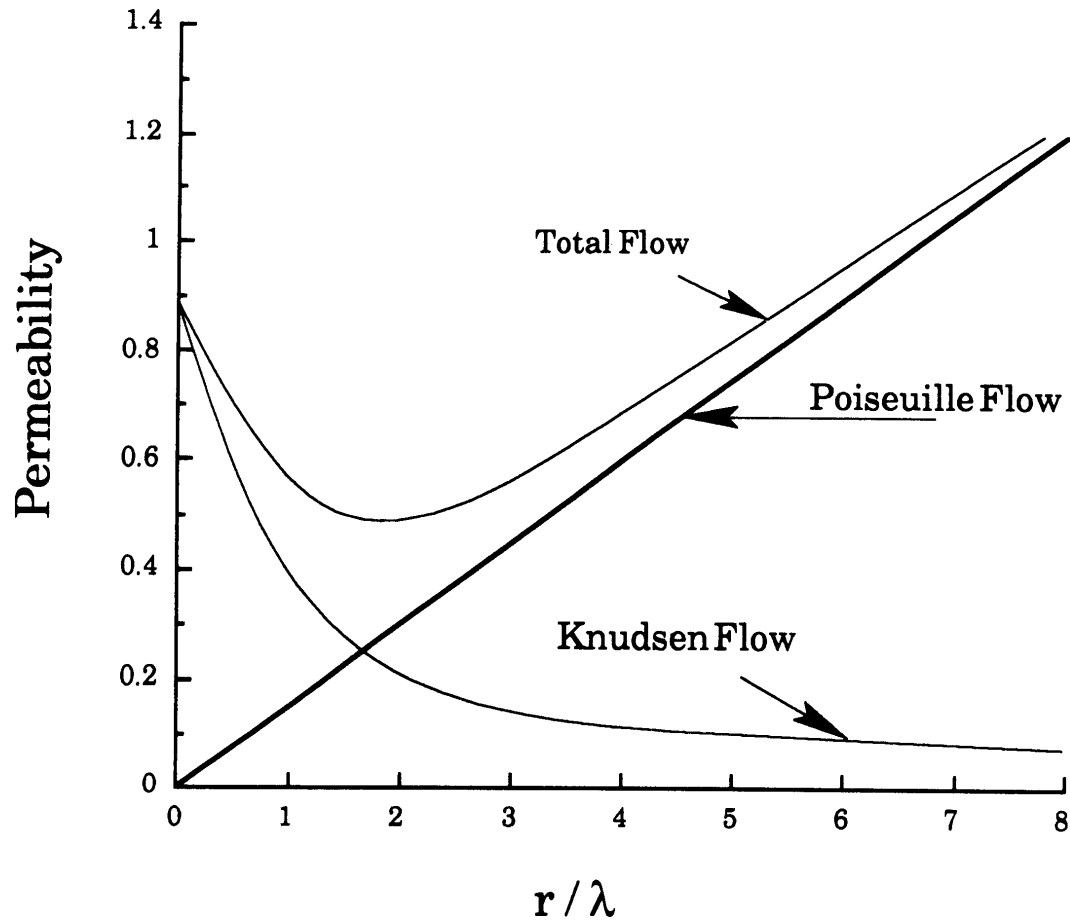


Figure 2.4.1.1 Total Flow in Porous Membranes Consists of Knudsen and Poiseuille Processes¹⁶⁸

independently, they will reach a speed of travel called the mean molecular velocity, μ , which is defined as

$$\mu = (8RT/\pi * M)^{1/2} \quad \text{Equation 2}$$

where R, T and M are as defined above. Equation 2 reveals that the mean molecular velocity is observed to be a function of molecular weight. In fact, the ideal separation factor for gases of different molecular weights is given by α , the square root ratio of the molecular weights of the gases;

$$\alpha = [M_2/M_1]^{1/2} \quad \text{Equation 3}$$

where subscripts 1 and 2 denote gases of different molecular weights.¹⁶⁹

Although Knudsen gas flow is used in some specialty applications,^{170,171} its utility has been inherently limited due to the low gas concentrations required. A good example which demonstrates the magnitude of the energy and time required for separating molecules of similar molecular weights by Knudsen flow is given by Kesting and Fritzsche, who state that American diffusion plants utilized 10,276 stages for the separation of $U^{235}F_6$ from $U^{238}F_6$ because the separation factor for these molecules is 1.0043.¹⁶⁸ Thus, the inefficiency of Knudsen flow through porous membranes for separating large volumes of gases led to the development of dense membranes.

2.4.2 Dense Membranes

Dense membranes have a significant advantage over porous membranes when applied to selective gas separation applications which is a direct result of the fundamental difference of penetrant/matrix interactions. As described above, the separation factor of porous membranes depends on the molecular weight ratio of the two gases. For dense

membranes, the separation depends on the difference in gas permeation which is a function of the particular physiochemical interactions experienced by each gas species within the polymer membrane.

The two major types of dense film membranes are: rubbery, which operate above their glass transition temperature (T_g); and glassy, those which operate below their T_g . It has been noted that the mode of gaseous transport is quite different in the glassy state when compared to the rubbery state. This section will first focus on gas permeation behavior in rubbery materials, which will serve as a foundation for a similar treatment of glassy materials. Predictive techniques for gaseous transport in polymers will also be reviewed.

2.4.2.1 Rubbery Polymers (Elastomers)

2.4.2.1.1 Theory of Gas Permeation

Rubbery polymers are capable of rubbery-type flow at temperatures above T_g . Recall that the T_g is the temperature interval where macromolecules experience increasing cooperative segmental motion along the backbone. Hence, elastomers above T_g have increased molecular motion as compared to glassy polymers.

Henry's Law (Equation 4) applies to elastomers permeated by low concentrations of supercritical gases (e.g. H_2 , O_2 , N_2).¹⁷²

$$C = S \cdot p \quad \text{Equation 4}$$

In Equation 4, C =the concentration of gas in the polymer (cc(STP)/cc polymer), S =Henry's solubility constant for a given gas/poly pair (cc(STP)/(cc polymer cmHg), and P =gas pressure in cmHg. Thus, the concentration of gas in the polymer increases with increasing gas pressure. It is interesting how this concentration changes across a membrane under applied pressure. Figure 2.4.2.1.1 depicts the process of a penetrant molecule migrating from the high-pressure interface to the low-pressure interface. The

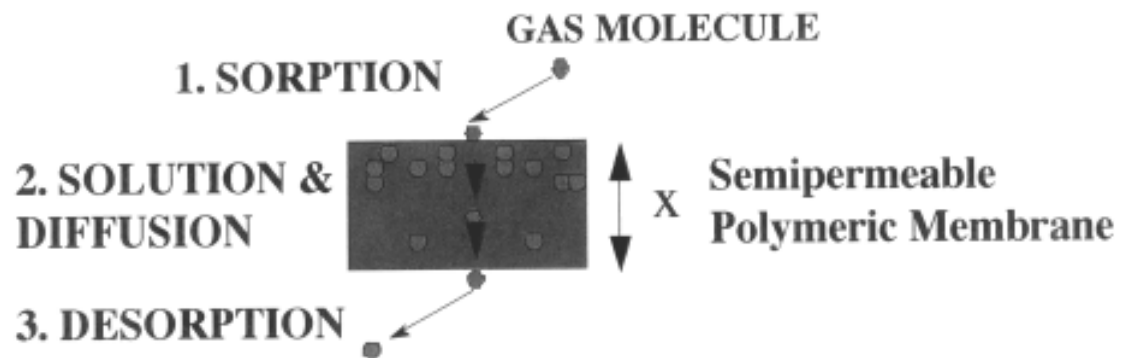


Figure 2.4.2.1.1.1 Gaseous Diffusion Across a Semipermeable Membrane

concentration of gas at any point in the membrane is given as (dC/dx) . Using this expression a total flux or rate of gas permeation, J , can be defined¹⁷³ as

$$J = D(dC/dx) = [\text{cm}^2/\text{sec}] \quad \text{Equation 5}$$

where D is the diffusion coefficient. By integrating with respect to C and x , and utilizing Henry's Law, the more commonly known of the flux equation¹⁷³ can be developed (Equation 6).

$$J = P^*(p_h - p_l)/x \quad \text{Equation 6}$$

Here, P =permeability coefficient or permeability, p_h =gas pressure on the high-pressure side of the membrane, p_l =gas pressure on the low-pressure side of the membrane, and x =membrane thickness. The permeability coefficient is thus a product of the diffusion coefficient and the solubility constant (Equation 7).¹⁷⁴

$$P = D*S \quad \text{Equation 7}$$

This equation is frequently invoked for gas permeation through semipermeable membranes. Before proceeding any further it is worth defining the gas separation selectivity for a gas pair, which is as follows:

$$\alpha_{A/B} = P_A/P_B = [D_A/D_B]*[S_A/S_B] \quad \text{Equation 8}$$

where $\alpha_{A/B}$ is the ratio of the permeability of gas A to gas B.¹⁷⁴ A diffusive and solubility selectivity can also be defined as $[D_A/D_B]$ and $[S_A/S_B]$, respectively. In the literature, it is common to report the permeability of a particular gas through a polymer membrane, as well as the membrane's selectivity with regard to that gas in the bicomponent mixture.

Clearly, it would be desirable to combine both a high selectivity and a high permeability for a single polymer, since that would allow one to obtain large volumes of pure gas.

Permeability is the product of the diffusion coefficient and the solubility constant. The temperature dependence of these parameters is an important issue. It has been found that each of these parameters have the following dependence on temperature,¹⁶⁸

$$D = D_0 * e^{-E(D)/RT} \quad \text{Equation 9}$$

$$P = P_0 * e^{-E(P)/RT} \quad \text{Equation 10}$$

$$S = S_0 * e^{-\Delta H(S)/RT} \quad \text{Equation 11}$$

where $E_d=(E(D))$ =apparent activation energy of the diffusion process, $E_p=(E(P))$ =apparent activation energy of the permeation process, $\Delta H_s=(\Delta H(S))$ =molar heat (enthalpy) of solution, and P_0 , D_0 , and S_0 are preexponential factors. Combining Equations 9-11 allows one to define Equation 12, as follows:

$$E_p = E_d + \Delta H_s \quad \text{Equation 12}$$

where E_p depends on the magnitude of E_d and ΔH_s . E_d is always positive and therefore the diffusion always increases with temperature. The thermodynamic parameter ΔH_s , on the other hand, can be positive or negative, depending on the polymer-gas interactions.¹⁷² The apparent activation energy of permeation is therefore a function of the specific polymer gas interaction.

2.4.2.1.2 A Physical Description of Gas Permeation

Thomas Graham postulated a mechanism in 1866 for the transport of gas molecules through a semipermeable membrane.¹⁷⁵ This mechanism contains three steps: the solution of the gas flows onto the upstream (high-pressure) surface of the membrane, gas diffuses through the membrane, and finally, gas evaporates from the downstream (low-pressure) surface of the membrane. This early description of gaseous transport is considered to be the basis for today's "solution-diffusion model", which is used to explain many membrane separations.¹⁷⁶

The solution and evaporation processes at either face of the membrane take place much more rapidly than does the gas transport through the membrane. The rate-determining step of the overall process is gas permeation through the membrane. Permeation is a function of two parameters: the solubility constant, S , and the diffusion coefficient, D . The solubility constant is a thermodynamic term based on the specific polymer-penetrant interactions and the condensibility of the penetrant, and the diffusion coefficient is a kinetic term referring to the movement of gas molecules inside the polymer matrix.¹⁷⁴ Although there is ongoing discussion with regard to what the polymer chains are actually doing, there is general agreement that the chains are sufficiently perturbed during this process to allow a penetrant molecule to reside between chains. The migration of gas molecules diffusing across the membrane requires energy in order to develop a location in the membrane downstream that is dimensionally favorable for the gas molecule. Stated another way, the diffusion coefficient determines "how frequently, on a time-averaged basis, a hole of sufficient volume appears next to the gas penetrant, enabling it to jump further through the membrane".¹⁶⁸ From this description of molecular diffusion it can easily be seen that an increase in chain backbone rigidity and/or intersegmental packing, which leads to a tighter structure and hindered bond rotation, will decrease the diffusion coefficient.¹⁷⁷

A rubbery polymer functioning as the gas-separating medium under Henry Law conditions, where both S and D are constants,¹⁷² can be relatively easy to describe compared to the transport of penetrants through a non-equilibrium state glassy polymer. Differences in the two states will be addressed in the following sections.

2.4.2.2 Glassy Polymers

2.4.2.2.1 Theory of Gas Permeation

The process of gaseous diffusion in glassy polymers is known to be more complex than that of rubbery polymers. The reason lies in the inhomogeneity which is due to “intersegmental packing defects frozen into the structure” when the temperature drops below the T_g .¹⁶⁸ The heterogeneity of glassy polymers result in deviations from Henry’s Law with respect to linear dependence of concentration versus applied pressure. Two types of sorption sites have been introduced to account for this non-linearity.¹⁷⁸ The first is called “Henry’s site” and the second is known as “Langmuir’s site”. Molecules in a Henry-type site obey Henry’s law and reside in the normally densified regions of the polymer. Molecules in a Langmuir-type site do not obey Henry’s law and reside either in microvoids (excess free volume frozen into the matrix) or “any mechanism which immobilizes penetrant molecules in a heterogeneous medium”.¹⁷⁹ Molecules in these sites are much less mobile than the ones in Henry-type sites. Local equilibrium exists between molecules in Henry and Langmuir sites. The description of gas sorption and diffusion through glassy polymers utilizing two different sites has become known as the “dual-mode sorption theory”.¹⁸⁰

Since solubility can either occur in Langmuir sites, C_H , or Henry sites, C_D , the overall solubility now becomes

$$C = C_D + C_H \quad \text{Equation 13}$$

where C is the total solubility. A molecule in a Henry site obeys solubility as defined by Equation 14, but the solubility of a molecule in a Langmuir site shows a non-linear dependence on pressure, as shown in Equation 15

$$C_D = S \cdot p \quad \text{Equation 14}$$

$$C_H = [C'_H * b * p] / [1 + b * p] \quad \text{Equation 15}$$

where C'_H = the hole saturation constant (a measure of sorption capacity) and b = characterizes the tendency for a penetrant to sorb into the Langmuir site (' b ' is lower for smaller molecules). Therefore, for glassy polymers the solubility is no longer a constant but a function of pressure, penetrant size, and the concentration of Langmuir sites.

If Henry's law conditions are not met, as in the case for glassy systems, the diffusion coefficient is no longer constant but becomes a function of thermal history and position in the membrane.^{181,182} Others have extended this theory by noting that sorbed penetrants in Langmuir sites may not be totally immobilized.¹⁸³⁻¹⁸⁵ This is still an active area of research¹⁸⁶ and has been called the "dual-mode transport theory".¹⁸⁷⁻¹⁸⁹

2.4.2.2.2 *A Physical Description of Gas Permeation*

The mechanisms for gas transport through glassy polymers are incompletely understood when considered on a molecular level. This is partially due to the inability to investigate individual molecules as they traverse the matrix. Although significant progress has been made in defining some mechanisms which describe penetrant passage, these models apply to only a select number of polymer/gas systems.¹⁷² As a result, a number of statistical models have been developed to explain the transport mechanism and estimate the parameters P , D and S .^{190,191} Most of the theoretical transport models found in the literature contain one or more adjustable parameters which are experimentally obtained.¹⁷² Additionally, expressions for gas diffusion coefficients, permeability coefficients and activation energies have been derived from "free-volume, statistical-mechanical, energetic, structural, or other considerations".¹⁷² Some of these models/derivations are described in references 182,192-196. One of the most popular concepts for modeling gas permeation is based on the available free-volume or "empty" volume of the system, which can be related to the penetrant concentration in the matrix.¹⁹⁷⁻²⁰⁰ This type of model suggests that gas permeability not only varies with free-

volume, which can be estimated by group contribution methods,^{201,202} but also with the free-volume distribution, which until now has been difficult to ascertain. Recently, macromolecular structure has been successfully probed using positron annihilation to determine the free-volume distribution.^{203,204} In the future, it would be quite instructive to compare this experimental data with that obtained from computer simulated calculations of the free-volume distribution.

2.4.3 Predictive Techniques for Gaseous Transport in Polymers

2.4.3.1 Empirical Correlations

A body of experimental data on gaseous diffusion through polymeric membranes has become available over the past several decades. Salame, a pioneer in this area, has developed a method for correlating this data through group contributions to permeability.^{205,206} He has defined a method which involves a parameter called a permachor (π) defined as

$$\pi = -(2.3/S) * \log (P/P^*) \text{ Equation 16}$$

where P^* is permeability of N_2 in natural rubber, P is permeability of N_2 in the test polymer, and S is the scaling factor. Salame and others have been moderately successful in predicting trends in polymer permeabilities. However, polymers that have been projected to be identical with respect to oxygen permeation were also predicted to have equal selectivity when using Salame's method.²⁰⁷

More recently, Park and Paul have correlated this data by using an empirical modification of a free volume scheme.²⁰⁸ Unlike the permachor calculations, their method does not require a scaling factor which incorporates an experimental density or an estimate of the occupied volume from a group contribution method. This new method may significantly improve the accuracy predicting and correlating gas transport properties of glassy polymer membranes.²⁰⁸

Robeson et al.²⁰⁹ has derived a procedure for predicting gas permeation behavior for aromatic polymers, such as polysulfones, polycarbonates, polyarylates, poly(aryl ketones) and poly(aryl ethers), which utilizes Equation 7,

$$\ln P = \sum_{i=1}^n (\phi_i \ln P_i) \quad \text{Equation 17}$$

where P =permeability, ϕ_i =volume fraction of a structural unit i and P_i =the permeability contribution of the structural unit. Using existing data and Equation 17, solutions can be generated for a particular system by using a least squares fit. The molar volume contributions can be calculated using a computer software program. Excellent agreement between predicted and experimental values for P have been reported.²¹⁰ In the future, this technique will be extended to other systems, such as polyamides and polyimides.²⁰⁹

2.4.3.2 Molecular Modeling via Computer Simulations

Computer simulation is a key to discovering a wealth of useful knowledge for many disciplines. As a really extreme example, Hawkings, a well known astrophysicist, has dedicated his life to developing the Unification Theory which he believes will allow him and others to predict the outcome of future events based on an accurate and detailed historical record.²¹¹

Currently, there is no widely accepted method for predicting gas-selecting properties beyond that of applying previously determined trends or estimates based on subsegment contributions. In gas permeation science, the “holy grail” or key to unlocking total structure/property relationships, is computer-aided molecular modeling which attempts to probe specific motions of both the penetrant and matrix using the known intra- and intermolecular forces of each.¹⁹⁴

The earlier computer aided descriptions of gas transport processes predicted diffusion coefficients and the activation energies for diffusion.^{196,212} More recently, advances in computer simulations have shed greater light on the overall transport process individual penetrants. The following section will present some of the more recent

advances in this area, in which more progress has been made for rubbery polymers than for glassy polymers. This is due to the relatively longer computational time needed to simulate the non-equilibrium thermodynamic state intrinsic to diffusion through a glassy system.

2.4.3.3 Recent Advances in Molecular Modeling

The area of computer simulated modeling of gaseous transport through dense membranes is very new. The first reported work is attributed to Shah et al. in 1989 in which he and coworkers estimated the fractional free volume available to spherical penetrants within polypropylene and poly(vinyl chloride) matrices.²¹³ Since 1989, significant discoveries have been made using molecular dynamic simulations on several structurally “simple” polymers (e.g. polyethylene,^{214,215} atactic polypropylene^{216,217} and polyisobutylene^{218,219}) as well as on more “complicated” ones such as polycarbonate,²²⁰ polystyrene,²²¹ and polyimides.^{222,223}

During 1990, Takeuchi utilized molecular dynamic simulations to show the migration path (or “jump”) of an oxygen molecule through a glassy -CH₂- matrix. The simulation was based on migration from one low energy site to another through a channel, which required an energy of activation (Figure 2.4.3.3.1).²²⁴ Similarly, Smit et al. in 1992 described a similar movement of CO₂ through a polyimide systems (Figure 2.4.3.3.2).²²³ In both of these examples, a channel is initially formed which lowers the energy barrier for migration. Afterward, the channel collapses and traps the penetrant in a new cavity.²²⁴ These two examples, as well as many others, strongly suggest that part of the gas diffusion mechanism consists of molecules “jumping” successively through lower energy sites within the polymer matrix.

Zhang et al. published some insightful work in 1995 based on molecular dynamic simulations for a polyimide interacting with O₂ and N₂ in the bulk.²²² The simulations enabled determination of the number of times O₂ interacted with different functional sites on the polymer backbone. Although this approach needs to be further developed, it has

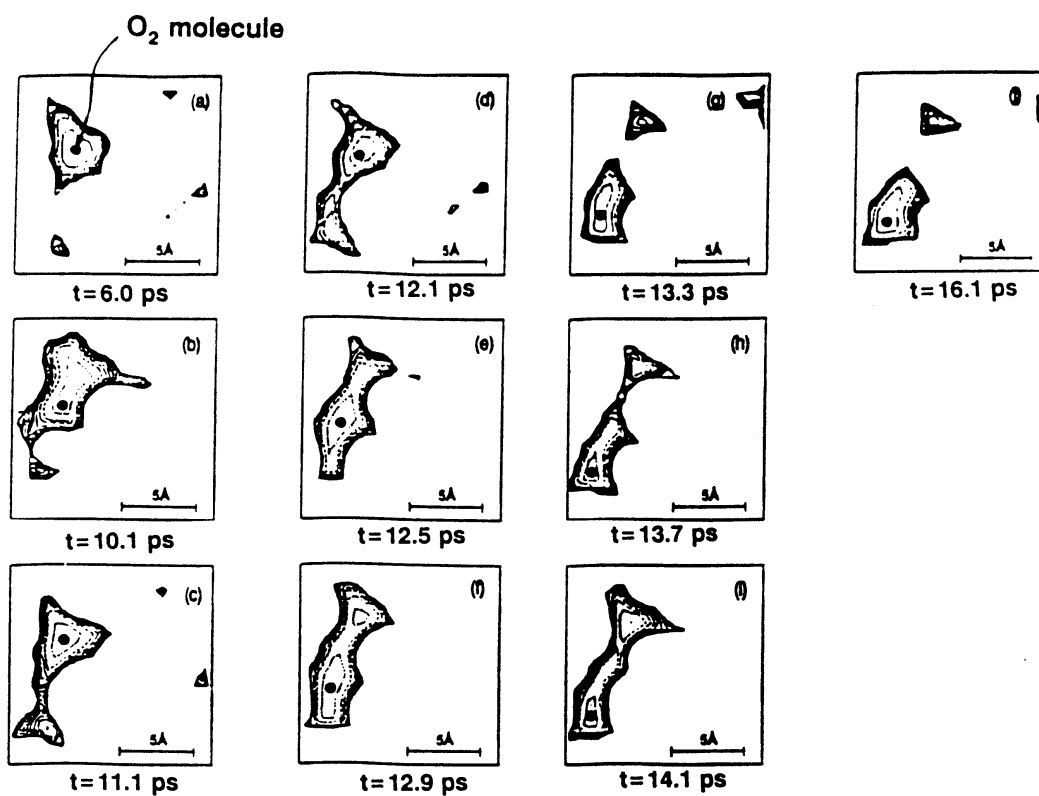


Figure 2.4.3.3.1 Molecular Dynamic Simulations of a "Jump" of an O_2 Molecule in a Glassy $-CH_2-$ Matrix. Changes in the Potential Energy Surfaces of "Cages" Enclosing the Penetrant Molecule²²⁴

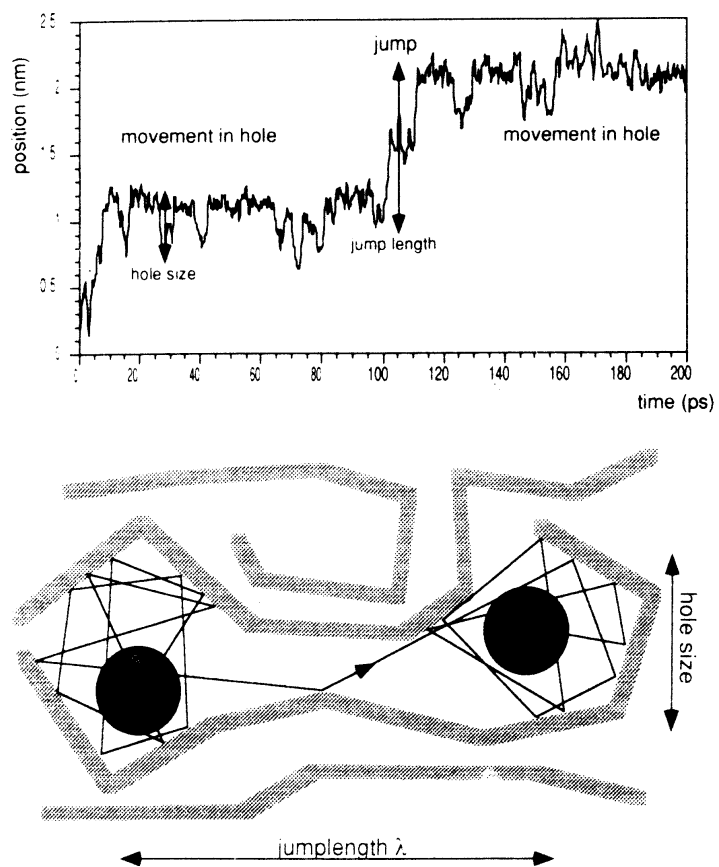


Figure 2.4.3.3.2 Movement and “Jump” of CO₂ Molecules Inside the Matrix of 6FDA-4,4’-PDA Polyimide²²³

the exciting possibility of elucidating specific interaction of gas penetrants throughout a polymeric system.

There is also an ongoing search for estimation methods that do not require large amounts of computer time. One example is the multidimensional transition state theory (TST) which studies the elementary jumps needed for a penetrant to traverse a glassy polymer.^{225,226} This approach “determines spatial fluctuations in the accessible volume for a particular penetrant” and uses these fluctuations to determine the adjustable parameters in the transition state theory.²²⁷ This method has the advantage of ignoring “nonjump” motions, thereby simplifying calculations and reducing the amount of computational time.²²⁶

For other examples of computer simulated modeling of gaseous transport, or computer simulations in general, see References 228-230.

2.4.3.4 The Current State of the Art

Since the 1960's, membrane separation of gases has progressed from being merely a laboratory curiosity to serving a large scale commercial need for purified gases. From this beginning until the early 1990's, hundreds of permeation measurements have been reported for a number of important polymer structures from aliphatic rubbers to glassy aromatic materials.

In 1991, Robeson²³¹ reported trends that he found to be applicable to all permeation measurements. He observed that, regardless of the repeat unit, polymer gas transport properties did not exceed a certain boundary level when viewed on a $\log(\alpha_{A/B})$ versus $\log(P_A)$ plot, where A is the faster permeating gas. This boundary is defined as the “upper bound”, which is the upper limit of gas separation performance for current state of the art membranes (Figure 2.4.3.4.1).²³¹ As membrane technology improves, it is likely that this bound will shift further upward.

Robeson also investigated the respective contributions of D and S to P.²³¹ Figures 2.4.3.4.2 and 2.4.3.4.3 show plots of S_{He}/S_{N_2} and D_{He}/D_{N_2} , the product of which is P_{He}/P_{N_2} . (Equation 18)

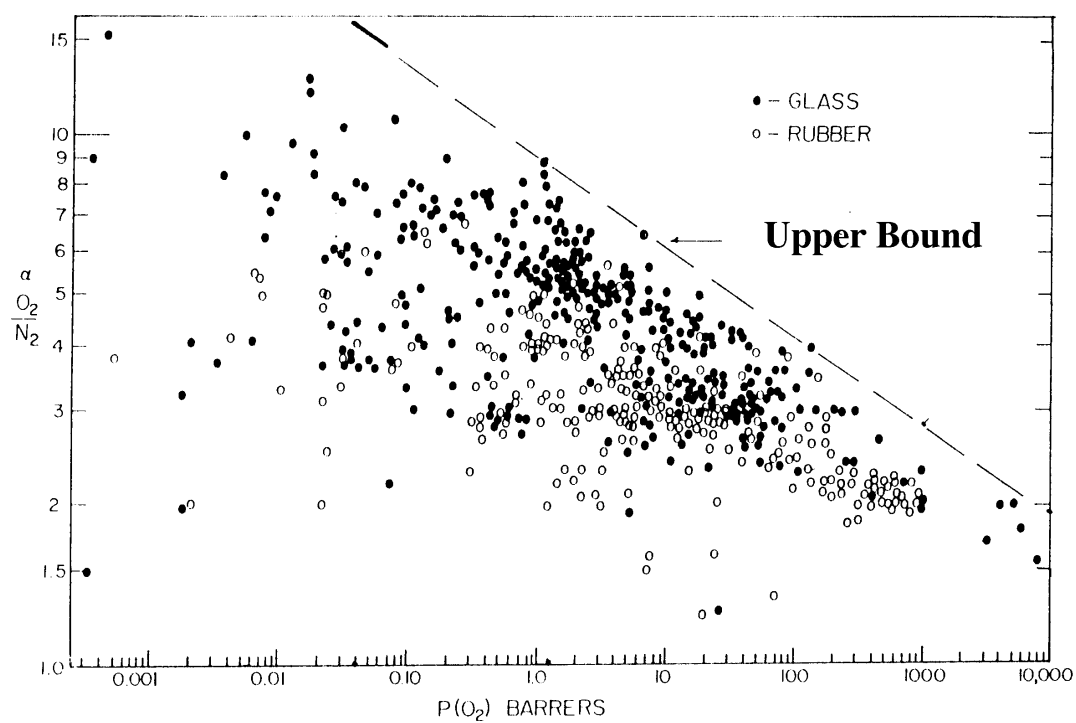


Figure 2.4.3.4.1 Log ($\alpha(O_2/N_2)$) vs. Log ($P(O_2)$). The Current State of the Art Polymers for Gas Selectivity Defines an Upper-Bound²³¹

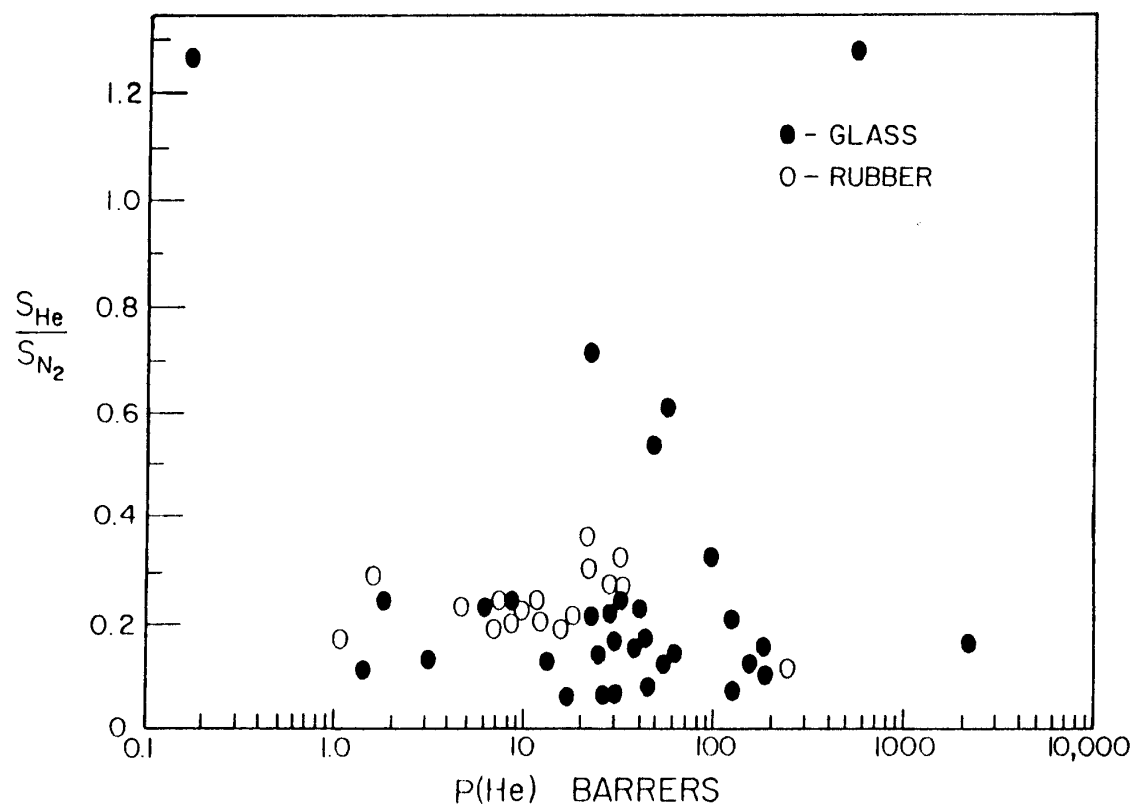


Figure 2.4.3.4.2 $S_{He}/S_{N(2)}$ vs. $\text{Log}(P_{He})$ ²³¹

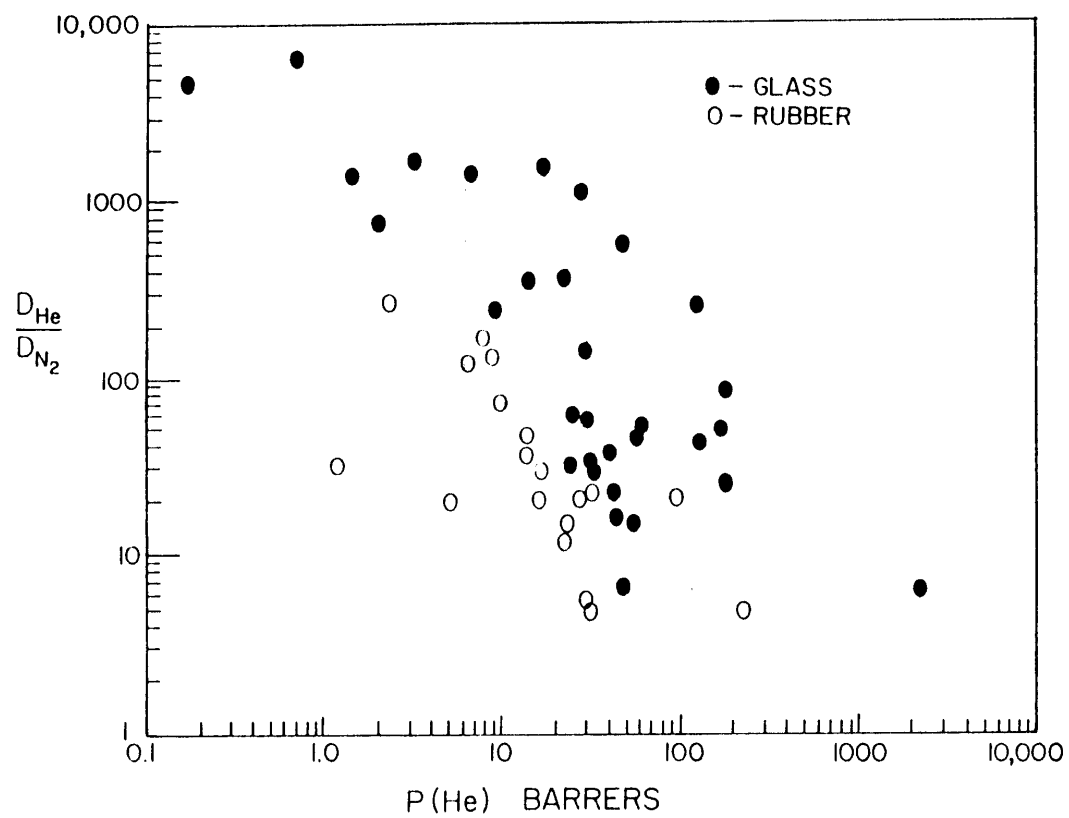


Figure 2.4.3.4.3 $\text{Log } (D_{\text{He}}/D_{\text{N}(2)})$ vs. $\text{Log } (P_{\text{He}})^{231}$

$$\alpha = P_{\text{He}}/P_{\text{N}_2} = (D_{\text{He}}/D_{\text{N}_2})*(S_{\text{He}}/S_{\text{N}_2}) \quad \text{Equation 18}$$

The solubility constant ratio as plotted against P_{He} shows very little variation, ranging from 0.05-0.35 for the majority of the data points. The few points having a ratio greater than 1.2 are most likely due to anomalous behavior.²³¹ In comparison, the plot of $D_{\text{He}}/D_{\text{N}_2}$ versus P_{He} shows a wide range of values from 5-7,000. This illustrates that the primary factor contributing to the overall permeability selectivity is the diffusive selectivity. This is also true for many other gas pairs in addition to He/N₂.

2.5 Structure-Property Relationships in Selective Gas Separation

A major objective in macromolecular science is to properly design and optimize the polymeric repeat unit, since this allows one to selectively tailor certain material properties. The relationship between the microscopic and macroscopic properties of a material is also called the “structure-property” relationship. Gas permeation science investigates inter- and intra-chain interactions of the polymer with respect to penetration by gas molecules, and on the microscopic level it is a sensitive probe to slight modifications in molecular structure.

There is a general relationship reported in the literature that as the permeability of gas A increases, its selectivity decreases.²³² This behavior is easily understood if the matrix is capable of tightly packing since the free volume, or unoccupied space, is reduced thereby decreasing its ability to transport permeants. Concurrently, the same material shows an improved “sieving” or higher selecting ability between gases of different sizes, shapes and electronic environments. While this general trend is true of polyimides, as well as most other polymers, there is a continuing goal to synthesize materials which can simultaneously achieve both higher permeability and higher selectivity, or which can attain higher permeability with only a slight reduction in selectivity. Two criteria have emerged to guide synthetic researchers in improving the permselectivity of membranes,²³³⁻²³⁶ which have evolved through extensive experimentation:

1. inhibition of intersegmental packing while simultaneously inhibiting intrasegmental (backbone) mobility
2. weakening interchain interactions (reduction of charge transfer complexes)

A proper application of these two principles may lead to membrane permselectivity above that defined by Robeson's concept of "upper bound".²³¹ This chapter reviews methods that have been employed which incorporate these principles.

2.5.1 Repeat Unit Design to Increase Permeability and Selectivity

Polyimides containing a $-C(CF_3)_2-$ link ('6F') in the repeat unit (eg. 6FDA) have been found, in many cases, to increase both the selectivity and permeability.^{237,238} Three primary reasons why this is true have been suggested.²³⁹ Incorporation of a large bulky group into the backbone inhibits the intrasegmental mobility due to the greater energy needed to rotate around the Ph-C bond, which is sterically hindered by the Ph-H/ CF_3 interaction (Figure 2.5.1.1). Not only do the '6F' groups increase chain stiffness, but they also act as molecular spacers to decrease chain packing, resulting in a polymer with greater free volume. Finally, as a result of reduced chain packing, the tendency to form charge transfer complexes (CTCs) is weakened or even eliminated. A decrease in CTCs increases the permeability and can be visually detected by the disappearance of color.²⁴⁰ Dianhydrides incorporating '6F' are generally more effective at enhancing selectivity versus comparable diamines containing '6F' groups. A dianhydride which has been found to behave similarly to 6FDA, called bis(phenylcarboxylic dianhydride) dimethylsilane, has been shown to increase permeability without significantly decreasing selectivity.²⁴¹

Pendant alkyl groups^{242,243} have also shown the ability to restrict intramolecular rotation while maintaining a highly rigid structure (Table 2.5.1.1).²⁴² Interestingly, the solubility selectivities for these materials remain relatively constant (1.2-1.3), while the range in the diffusive selectivities is quite wide, from 2.7 to 5.0. It is also evident that by increasing the bulkiness of the diamine with an increasing number of methyl substituents, the diffusive selectivities decrease as a result of greater free volume. In this case, although the permeability increases with each methyl substituent, the selectivity is reduced considerably.

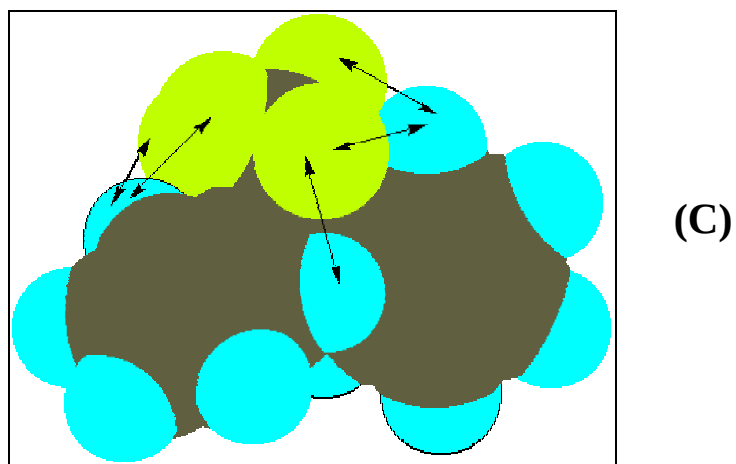
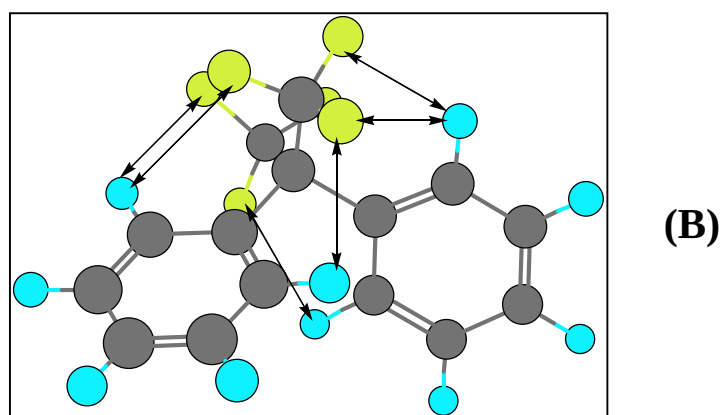
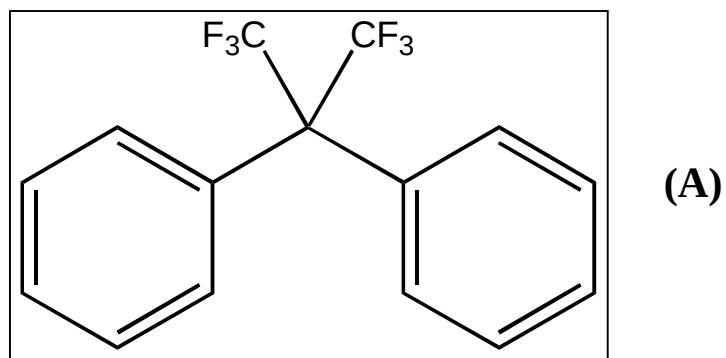
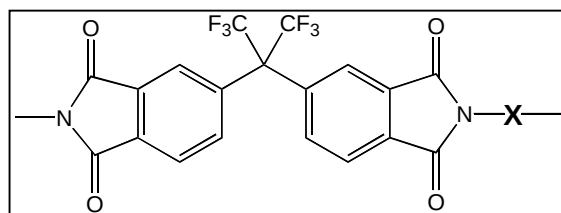


Figure 2.5.1.1 6F Biphenyl Showing Steric Hinderance Between Ph-H's and F's (A) 2-Dimensional (B) 3-Dimensional , Ball and Stick (C) 3-Dimensional, Space Filling

Table 2.5.1.1 Effect of the Structure of Substituted Diamines in 6FDA Polyimides on Glass Transition Temperature, Permeability, Diffusion, and Solubility Coefficient Ratios for the System O₂/N₂²⁴²



-X-	<u>T_g (°C)</u>	<u>P(O₂) (Ba)</u>	<u>P(O₂)/P(N₂)</u>	<u>D(O₂)/D(N₂)</u>	<u>S(O₂)/S(N₂)</u>
	298	3.0	6.7	5.0	1.3
	335	11.3	5.0	3.9	1.3
	377	109	3.5	2.7	1.3
	351	4.2	5.3	4.3	1.2
	355	13.4	5.0	4.1	1.2
	420	122	3.4	2.8	1.2

Langsam and Burgoyne investigated ortho-alkyl diamines and their effect on restricting the C-N bond rotation (Figure 2.5.1.2).²⁴³ They demonstrated that an o-methyl substituted 9,9-bis(4-aminoaryl)fluorene condensed with 6FDA reduced in a 5 fold increase in O₂ permeability while O₂/N₂ selectivity only decreased by 8%. Polyimides having an ethyl instead of methyl substituent were shown to increase O₂ permeability and restrict rotational freedom, affording higher T_gs.²⁴³ Each of these observations can be rationalized by the restricting influence of the substituent on the rotational freedom about the imide C-N bond while concomitantly inhibiting intermolecular chain packing.

Several researchers have investigated using sulfone bridging units to achieve high permselectivities.²⁴⁴⁻²⁴⁶ Generally, sulfone linkages give high selectivity but low permeability. Kawakami et al.²⁴⁵ noted possible charge transfer complex formation with sulfones, which usually increases chain packing density and suppresses segmental mobility. The effect of polar substituents such as bromine,²⁴⁷ chlorine and fluorine²⁴⁸ have also been investigated. A polar substituent, such as bromine, is known to increase intersegmental attractions, which lead to high diffusive selectivities.²⁴⁷ Stern et al.²⁴⁹ recently reported permselectivity characteristics for a select number of 6FDA based polyimides in combination with phenolic containing diamines (Figure 2.5.1.3 and Table 2.5.1.2). In particular, the 6FDA/HAB homopolymer exhibited a considerable improvement in O₂/N₂ selectivity while maintaining good O₂ permeation.

2.5.2 *Meta versus Para Isomers*

Several researchers have reported on the differences observed by varying the diamine linkage from *meta* to *para*.²⁵⁰⁻²⁵³ It has been found that meta catenation tends to decrease permeability and increase selectivity due to impeded intra and intersegmental motion. One good comparison is between the two isomers, PMDA-4,4'-ODA (4,4') and PMDA-3,3'-ODA (3,3') shown in Figure 2.5.2.1.²⁵⁴ The 4,4' system has a T_g of 400°C compared with that of 280°C for the 3,3'-isomer. Based on this information alone, it may be surmised that the 4,4' isomer would have the lower permeability when compared to 3,3'. However, there may be other thermal transitions which may specifically influence

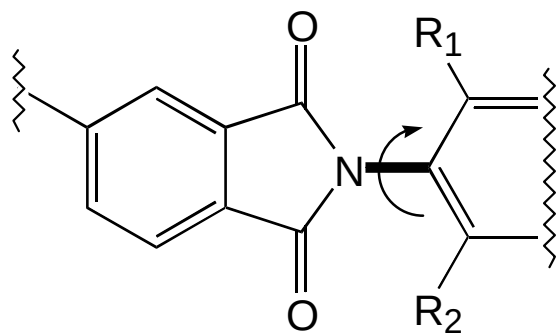


Figure 2.5.1.2 Effects of *ortho*-Substituents on C-N Bond Rotation²⁴³

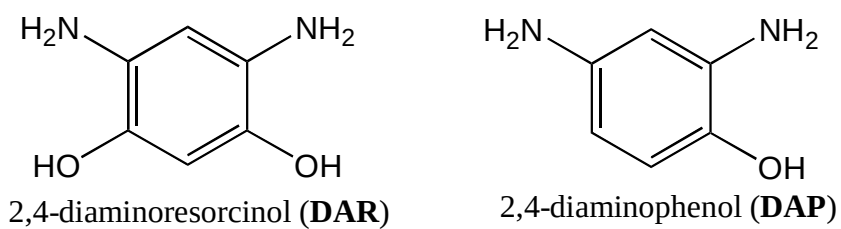
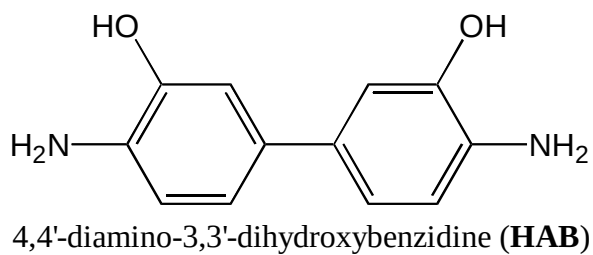


Figure 2.5.1.3 Hydroxyl-containing Diamine Monomers²⁴⁹

Table 2.5.1.2 Permeability for Hydroxyl-containing 5,5'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene] bis-1,3-isobenzene-furandione (6FDA) Based Polyimides²⁴⁹

System 6FDA/	Permeability	
	O(2) (Ba)	O(2)/N(2)
HAB*	1.6	9.3
HAB**	1.8	7.5
DAP	2.4	7.1
DAR	2.2	7.4

*thermally imidized-insoluble film

**chemically imidized-soluble

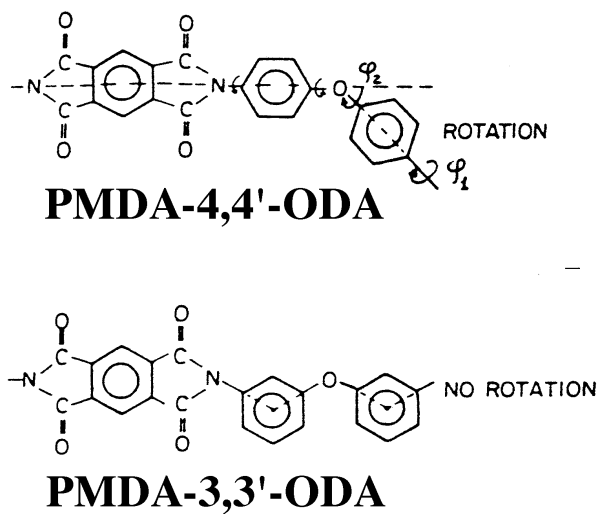


Figure 2.5.2.1 Differences in Intrasegmental (rotational) Mobility of Two Polyimide Isomers: PMDA-4,4'-ODA (*para*-isomer) and PMDA-3,3'-ODA (*meta*-isomer)²⁵⁴

Table 2.5.2.1 Effect of Diamine Isomers on Gas Permeability and Selectivity²³⁹

<i>Isomer</i>	P(O₂) Ba	P(O₂)/P(N₂)
PMDA-4,4'-ODA	0.22	4.5
PMDA-3,3'-ODA	0.13	7.2

gas separation characteristics. In fact, the 4,4' is twice as permeable when compared to 3,3' isomer. This is because, unlike the 4,4' species, the 3,3' isomer has no small-scale sub- T_g secondary relaxations due to restricted intrasegmental mobility in the glassy state (Table 2.5.2.1).²³⁹ Figure 2.5.2.1 visually depicts the rotational differences between the 4,4' and the 3,3' isomers.

2.5.3 Chemical or Electrostatic Crosslinking, and Annealing

A polymer with the appropriate chemical structure may undergo thermal and/or ultraviolet (UV) promoted crosslinking. Chemical crosslinks, in some cases, may promote an increase in selectivity while only moderately affecting the permeability. Recently, Rezac et al.²⁵⁵ reported a study of blends utilizing in-chain aliphatic diacetylene-functionalized polyimides with wholly aromatic non-reactive polyimides. Acetylene moieties are known to undergo thermal crosslinking at or above 240°C. The authors report both an increase in O₂ permeability and an increase in O₂/N₂ selectivity for crosslinked blends. Although they report values of O₂ permeability and O₂/N₂ selectivity were only 1.30Ba and 6.8, respectively, these might have been increased by employing a better base material in the blends. The base material consisted of 6FDA/bis(4-aminophenyl) isopropylidene. Rezac et al.²⁵⁶ have also reported on acetylene terminated polyimide/non-reactive polyimide blends which exhibit no appreciable change in permeability or selectivity after cure. The cured blends did show good solvent resistance. Polyarylates have also been investigated for their gas separation characteristics. Those containing in-chain benzocyclobutane units were crosslinked above 180°C.²⁵⁷ Unfortunately, apparent degradation led to an increase in permeability and a decrease in selectivity; the opposite of what is expected for simple crosslinking.

Ultraviolet irradiation is also known to promote crosslinking. Carbonyl group electrons, eg. in benzophenone, can be excited to a higher energy state when exposed to UV light. In the excited state, carbonyls can abstract labile protons from other species in the system (usually benzylic or methylene protons) to generate carbon based radicals. An intermolecular crosslink is formed when carbon bearing radicals from two chains

combine to form a chemical bond. Kita et al.²⁵⁸ and others²⁵⁹⁻²⁶¹ have recently reported on UV photocrosslinking of benzophenone containing polymers. Kita et al. reported that as the UV irradiation time was increased, the permeability decreased. The reduction in permeability was shown to be a result of a decrease in the diffusivity coefficient rather than a change in the solubility constant. Overall, impressive permselectivity values were reported (Table 2.5.3.1).

Electrostatic or ionomeric crosslinks have been explored. Chen et al.²⁶² reported on a series of polystyrenes with varying sulfonate content. It was observed that as the sulfonate content increased, lower permeabilities and higher selectivities resulted. This phenomenon was interpreted as resulting from electrostatic crosslinking. The selectivity coefficient for these materials varied with the counter ion, eg. Na^+ or Mg^{2+} , with the best combination of O_2/N_2 selectivity (11.7) and O_2 permeability (0.42 Ba) being obtained for Mg^{2+} with 27.5 mole percent sulfonation.

Electrostatic crosslinking via polyimides with pendant carboxylic acids^{249,263} and sulfonic acids²⁴⁹ have also been reported. Li et al.²⁶³ have compared polyimides containing 1,3-phenylene diamines with and without a carboxylic acid group in the 5-position. The T_g of the carboxylic acid containing polyimide was found to increase due to restricted rotation imposed by the bulky group and possible intermolecular electrostatic crosslinking. The fractional free volume of the polymer increased with the acid group and led to a higher permeability coefficient. In addition to a 20% higher O_2 permeabilities, higher O_2/N_2 selectivities were also reported (27%) for the carboxyl functionalized polyimides.

Increased permselectivity can be obtained with polymer membranes containing cobalt complexes due to facilitated transport of molecular oxygen.²⁶⁴⁻²⁶⁸ Chen et al.²⁶⁴ reported the permselectivity behavior of polycarbonate blended with Co(III) acetylacetonate (Co(acac)_3). For the system with 3wt% Co(acac)_3 there is a 13% loss in O_2 permeability and a gain of 28% in O_2/N_2 selectivity. Even though the reason for this favorable trade-off is not completely understood, it may be related to specific interactions between the carbonyls in the polycarbonate and the cobalt complex which were detectable

Table 2.5.3.1 Permeability coefficients for unirradiated and irradiated polyimide films at 35°C and 2 atm²⁵⁸

System	UV exposure Time (min)	Permeability		
		O(2) (Ba)	N(2) (Ba)	O(2)/N(2)
BTDA-TMPD*	0	9.84	1.79	5.5
	1	4.15	0.75	5.3
	10	0.48	0.04	14
	30	0.20	0.02	14
BTDA:6FDA(1:1)/ TMPD	0	12.3	2.73	4.5
	30	1.74	0.18	9.6
	60	1.58	0.15	11

*TMPD=2,4,6-trimethyl phenylenediamine

by FTIR. Ruaan et al.²⁶⁷ not only report an increase in O₂/N₂ selectivity but also an increase in O₂ permeability with their cobalt complex/polymer system.

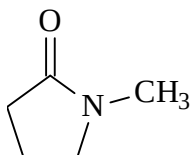
CHAPTER 3 EXPERIMENTAL

3.1 Materials

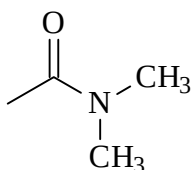
Solvent, monomer and reagent purity were obviously all important factors for the synthesis of high molecular weight polyimides. Therefore, purification of these materials was rigorous. Pure, anhydrous solvents were assured by distillation, either under vacuum or nitrogen, from a flask containing the solvent and a dehydrating agent. The glassware, monomers and reagents were also carefully purified and dried before use.

3.1.1 Solvents

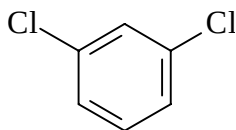
1-Methyl-2-Pyrrolidinone (NMP: Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under reduced pressure (~5 torr) (b.p. 205°C/760mmHg, 82°C/10mmHg).



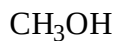
N,N-Dimethylacetamide (DMAc: Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under reduced pressure (~5 torr) (b.p. 163-165°C/760mmHg).



o-Dichlorobenzene (o-DCB: Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under reduced pressure (~5 torr) (b.p. 180°C/760mmHg).



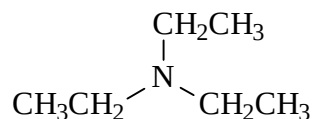
Methanol (Fisher Scientific) was received as an HPLC grade solvent and was used without further purification (b.p. 64.7°C/760mmHg).



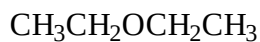
Ethanol (100%, AAPER Alcohol and Chemical) was used as received (b.p. 78.5°C/760mmHg).



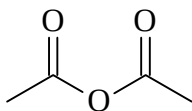
Triethylamine (TEA or NEt_3 : Fisher Scientific) was dried over calcium hydride for at least 12 hours prior to distillation under nitrogen (b.p. 88.8°C/760mmHg).



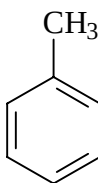
Diethyl Ether (OEt_2 : Anhydrous, Mallinckrodt) was used as received (b.p. 34.6°C/760mmHg).



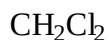
Acetic Anhydride (Aldrich) was stirred over calcium hydride for at least 12 hours prior to distillation under vacuum (~5 torr) (b.p. 138-140°C/760mmHg).



Toluene (Burdick and Jackson) was received as an HPLC grade solvent and was used without further purification (b.p. 110.6°C/760mmHg).



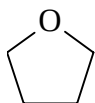
Dichloromethane (Aldrich) was used as received (b.p. 40°C/760mmHg).



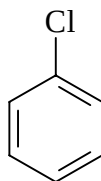
Chloroform (Burdick and Jackson) was received as an HPLC grade solvent and was used without further purification (b.p. 61-62°C/760mmHg).



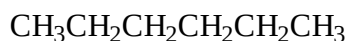
Tetrahydrofuran (THF: EM Science) was used as received (b.p. 76°C/760mmHg).



Chlorobenzene (Fisher Scientific) was received as a laboratory grade solvent and was used without further purification (b.p. 132°C/760mmHg).



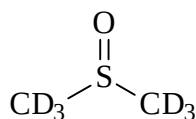
Hexane (Burdick and Jackson) was received as an HPLC grade solvent and was used without further purification (b.p. 69°C/760mmHg).



Deuterated Chloroform (CDCl_3 ; Cambridge Isotope Laboratories) was dehydrated over molecular sieves or alumina powder prior to use (b.p. 61°C/760mmHg).



Deuterated Dimethyl Sulfoxide (DMSO-d_6 ; Cambridge Isotope Laboratories) was dehydrated over molecular sieves or alumina powder prior to use (b.p. 55°C/5mmHg).



3.1.2 Monomer Purification

3.1.2.1 Diamines

1,3-Phenylenediamine (*m*-PDA)

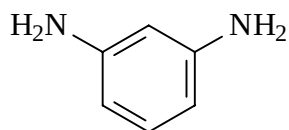
Supplier: Aldrich

Empirical Formula: $C_6H_8N_2$

Molecular Weight (g/mole): 108.14

m.p., °C: 66

Structure:



Purification: *m*-PDA was sublimed under vacuum (~5 torr) at ~65°C. *m*-PDA is photo- and air-sensitive and must be stored under vacuum and away from light.

5(6)-Amino-1-(4-aminophenyl)-1,3,3-trimethylindane (diaminophenylindane or DAPI)

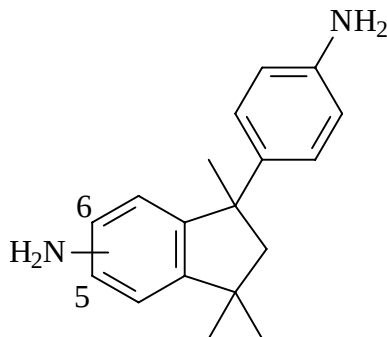
Supplier: Ciba

Empirical Formula: $C_{18}H_{22}N_2$

Molecular Weight (g/mole): 266.39

m.p., °C: 78-112

Structure: Equimolar mixture of C-5 and C-6 isomers as determined by HPLC.



Purification: DAPI was dried under vacuum (~5 torr) at ~50°C for more than 12 hours prior to use.

9,9-Bis(4-aminophenyl) fluorene (FDA)

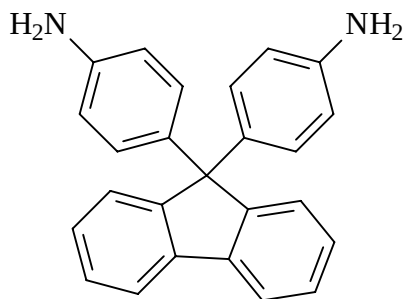
Supplier: Kennedy and Klim

Empirical Formula: $C_{25}H_{20}N_2$

Molecular Weight (g/mole): 348.16

m.p., °C: 235-237

Structure:



Purification: Monomer grade FDA was obtained and dried at ~75°C under vacuum (~5 torr) for at least 12 hours.

3,7-Diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)

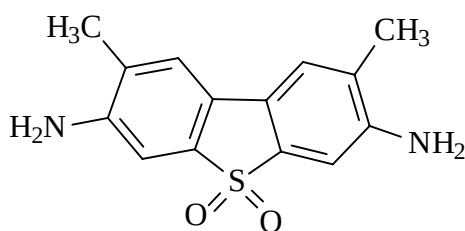
Supplier: Chriskev

Empirical Formula: $C_{14}H_{14}O_2N_2S$

Molecular Weight (g/mole): 274.34

m.p., °C: 360 (dec.)

Structure:



Purification: Monomer grade DDBT was obtained and dried at ~50°C under vacuum (~5 torr) for at least 12 hours.

2,2-Bis(3-amino-4-methylphenyl)-hexafluoropropane (Bis-AT-AF)

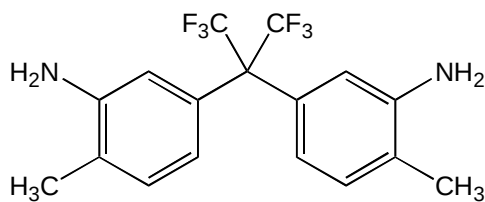
Supplier: Chriskev

Empirical Formula: $C_{17}H_{16}N_2F_6$

Molecular Weight (g/mole): 364

m.p., °C: 105-106

Structure:



Purification: Monomer grade BisATAF was obtained and dried at ~50°C under vacuum (~5 torr) for at least 12 hours.

2,2-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (Bis-AP-AF)

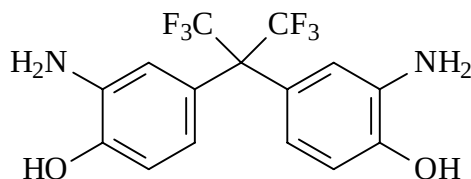
Supplier: Chriskev

Empirical Formula: $C_{15}H_{12}O_2N_2F_6$

Molecular Weight (g/mole): 366

m.p., °C: 240-243

Structure:



Purification: BisAPAF was recrystallized from ethanol. To a 500ml 3-neck flask equipped with a mechanical stirrer, nitrogen inlet/outlet and a condenser, 100g of BisAPAF was added along with 150ml of ethanol. The solution became homogeneous at reflux. To this solution, $CHCl_3$ was added until it became slightly turbid (~150ml). Upon cooling, the BisAPAF precipitated as a fine white powder which was filtered, washed with $CHCl_3$ and dried under vacuum (~5 torr) at 100°C for 24 hours (~87% yield).

3,3'-Dihydroxy-4,4'-diamino-biphenyl (HAB)

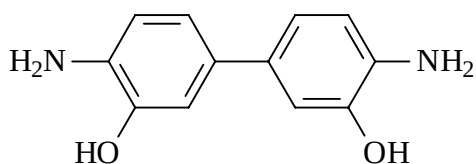
Supplier: Chriskev

Empirical Formula: $C_{12}H_{12}O_2N_2$

Molecular Weight (g/mole): 216.2

m.p., °C: 295-296

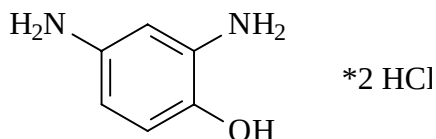
Structure:



Purification: Monomer grade HAB was obtained and dried at ~50°C under vacuum (~5 torr) for at least 12 hours.

2,4-Diaminophenol dihydrochloride (DAP)

Supplier: Aldrich
Empirical Formula: $C_6H_{10}ON_2Cl_2$
Molecular Weight (g/mole): 197.07
m.p., °C: 222 (dec.)
Structure:



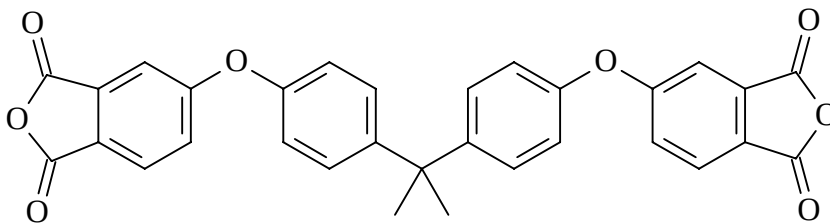
Purification: DAP was received as light pink flake of 98% purity. It was found to be monomer grade ($\geq 99.9\%$) after drying for it yielded high molecular weight polyimides. DAP was dried at room temperature under vacuum (~5 torr) for at least 12 hours.

3.1.2.2 Dianhydrides

2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bisphenol-A dianhydride or BPADA)

Supplier: General Electric Company
Empirical Formula: $C_{31}H_{21}O_8$
Molecular Weight (g/mole): 520.49
m.p., °C: 191-193

Structure:

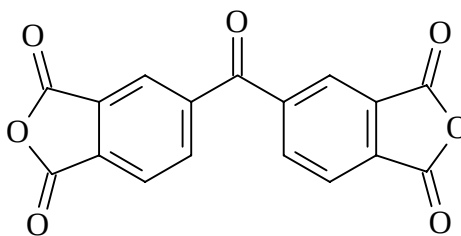


Purification: BPADA was recrystallized from a mixture of toluene and acetic anhydride. To a 1L 3-neck round bottom flask equipped with a mechanical stirrer, condenser and nitrogen inlet, 100g of BPADA, 500g of toluene and 50g of acetic anhydride was added. The mixture was heated to reflux yielding a homogeneous mixture. The mixture was allowed to cool overnight. The resulting solid BPADA was filtered and returned to the round bottom flask to which 500g of toluene and 10g of acetic anhydride was added. Again, this mixture became homogeneous at reflux and upon cooling afforded crystals of BPADA. The whole procedure was repeated again and yielded purified BPADA in about 70% yield (m.p. 191-193°C).

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA)

Supplier: Allco
Empirical Formula: $C_{17}H_6O_7$
Molecular Weight (g/mole): 322.23
m.p., °C: 224-226

Structure:



Purification: BTDA was obtained as a fine white powder and was dried under vacuum (~5 torr) at ~180°C for at least 12 hours prior to use.

3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA)

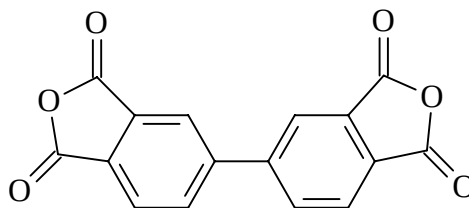
Supplier: Chriskev

Empirical Formula: $C_{16}H_6O_6$

Molecular Weight (g/mole): 294.00

m.p., °C: 300

Structure:



Purification: Polymer grade BPDA was obtained as a fine white powder and was dried at ~180°C for at least 12 hours under vacuum (~5 torr) prior to use.

1,2,4,5-Benzenetetracarboxylic dianhydride (PMDA)

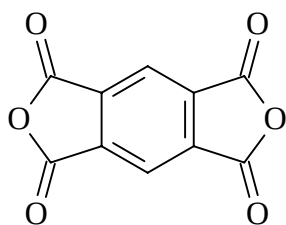
Supplier: Allco

Empirical Formula: $C_{10}H_2O_6$

Molecular Weight (g/mole): 218.12

m.p., °C: 286

Structure:



Purification: Polymer grade PMDA was obtained as a fine white powder and was dried at ~180°C for at least 12 hours under vacuum (~5 torr) prior to use.

5,5'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene] bis-1,3-isobenzene-furandione (6FDA)

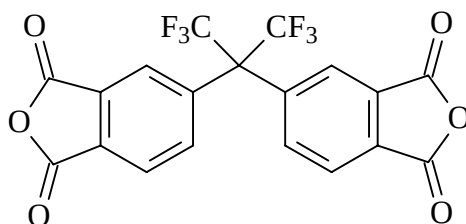
Supplier: Hoechst Celanese Corporation

Empirical Formula: $C_{19}H_6F_6O_6$

Molecular Weight (g/mole): 444.00

m.p., °C: 247

Structure:



Purification: Polymer grade 6FDA was obtained as a fine white powder and was dried at ~180°C for at least 12 hours under vacuum (~5 torr) prior to use.

4,4'-Bis[4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (biphenylether dianhydride or BPEDA)

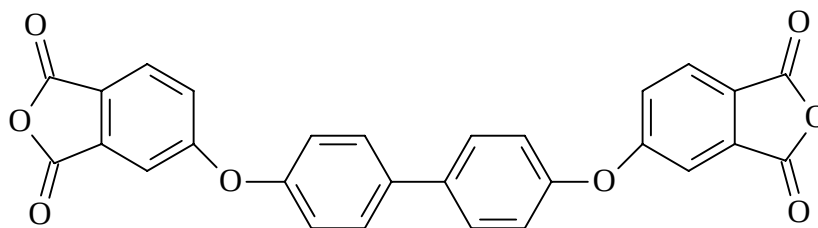
Supplier: General Electric Company

Empirical Formula: $C_{28}H_{15}O_8$

Molecular Weight (g/mole): 478.41

m.p., °C: 294-296

Structure:



Purification: Polymer grade BPEDA was dried at $\sim 180^\circ\text{C}$ for at least 12 hours under vacuum (~ 5 torr) prior to use.

Diphenylsulfone dianhydride (DSDA)

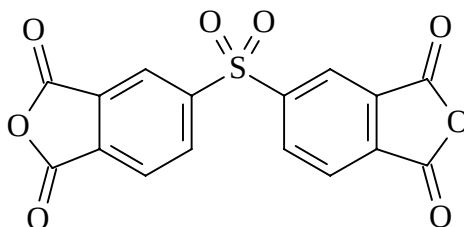
Supplier: Chriskev

Empirical Formula: $C_{12}H_6O_8S$

Molecular Weight (g/mole): 310.24

m.p., °C: 287-288

Structure:



Purification: Polymer grade DSDA was obtained as a fine white powder and was dried at ~160°C for at least 12 hours under vacuum (~5 torr) prior to use.

3.1.3 Endcap Purification

Phthalic anhydride (PA)

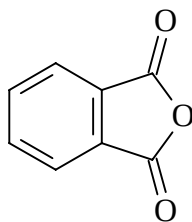
Supplier: Aldrich

Empirical Formula: $C_8H_4O_3$

Molecular Weight (g/mole): 148.12

m.p., °C: 134

Structure:



Purification: PA was purified by vacuum (~5 torr) sublimation at ~120°C.

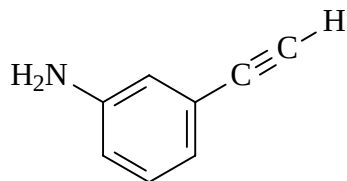
3-Ethynyl aniline (*m*-aminophenyl acetylene or *m*-APA)

Supplier: Acros

Empirical Formula: C_8H_7N

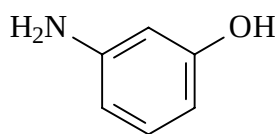
Molecular Weight (g/mole): 117.15

Structure:



***m*-Aminophenol (*m*-AP)**

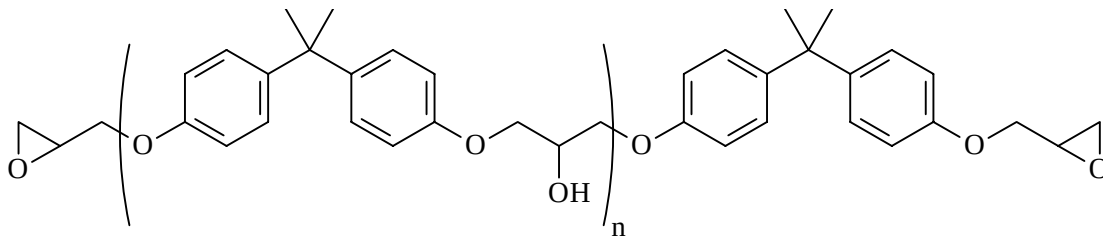
Structure:



3.1.4 Epoxy Resins

Bisphenol A epoxy resin (EPON 828)

Structure:



Purification: EPON 828 was used as received without further purification.

Tetraglycidyl bis-(p-aminophenyl) methane (MY721)

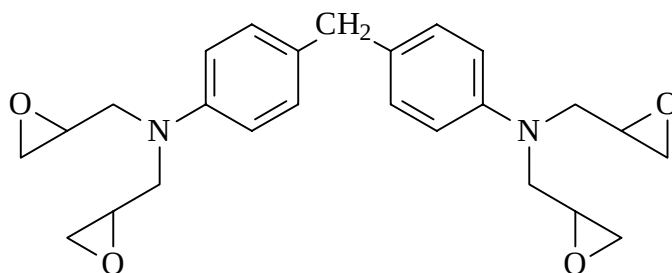
Supplier: Ciba Polymers

Empirical Formula: $C_{25}H_{30}O_4N_2$

Molecular Weight: 435.82

EEW(g resin/mole epoxide): 112.3

Nominal Structure:



Purification: MY721 was used as received without further purification.

3.2 Monomer Synthesis

3.2.1 Reagents

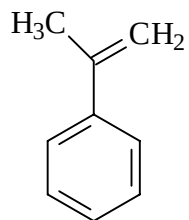
α -Methylstyrene (α -MS)

Supplier: Aldrich

Empirical Formula: C_9H_{10}

Molecular Weight (g/mole): 118.18

Structure:



Purification: α -MS was deinhibited (*p*-tert-butylcatechol) with basic alumina immediately prior to use.

Sulfuric Acid

Supplier: Mallinckrodt, 96.2%

Empirical Formula: H_2SO_4

Molecular Weight (g/mole): 98.07

Purification: Used as received

Nitric Acid

Supplier: Fisher, 69.5%

Empirical Formula: HNO_3

Molecular Weight (g/mole): 63.01

Purification: Used as received

Hydrazine Monohydrate

Supplier: Acros, 99%

Empirical Formula: $\text{H}_6\text{N}_2\text{O}$

Molecular Weight (g/mole): 50.06

b.p., $^{\circ}\text{C}$: 113.5/760mmHg

Structure:



Purification: Used as received

Palladium on Activated Carbon (Pd/C)

Supplier: Aldrich

Empirical Formula: Pd 10%, +C

Purification: Used as received

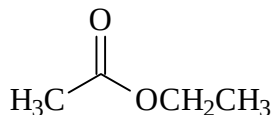
Ethylacetate (EtOAc)

Supplier: Mallinckrodt, 99.6%

Empirical Formula: $\text{C}_4\text{H}_8\text{O}_2$

Molecular Weight (g/mole): 90.09

Structure:



Purification: Used as received

Magnesium Sulfate, Anhydrous

Supplier: Mallinckrodt, Reagent Grade

Empirical Formula: MgSO_4

Molecular Weight (g/mole): 120.37

Purification: Used as received

Basic Alumina, Activated

Supplier: Aldrich, Standard Grade

Empirical Formula: Al_2O_3

Purification: Used as received

Sodium Bicarbonate

Supplier: EM Science

Empirical Formula: NaHCO_3

Molecular Weight (g/mole): 84.01

Purification: Used as received

4,4'-Isopropylidenediphenol (bisphenol-A)

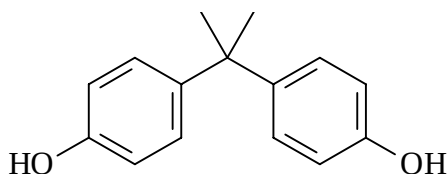
Supplier: Dow Chemical

Empirical Formula: $\text{C}_{15}\text{H}_{16}\text{O}_2$

Molecular Weight (g/mole): 228.29

m.p., °C: 158-159

Structure:



Purification: Bisphenol A was purified by recrystallization from toluene (Bisphenol A: toluene/ 1:5.3).

Sodium Hydroxide

Supplier: Mallinckrodt, Pellets, 99.4%

Empirical Formula: NaOH

Molecular Weight (g/mole): 40.00

Purification: Used as received

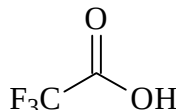
Trifluoroacetic Acid (TFAA)

Supplier: Fisher, Reagent Grade

Empirical Formula: $\text{C}_2\text{HO}_2\text{F}_3$

Molecular Weight (g/mole): 114.02

Structure:



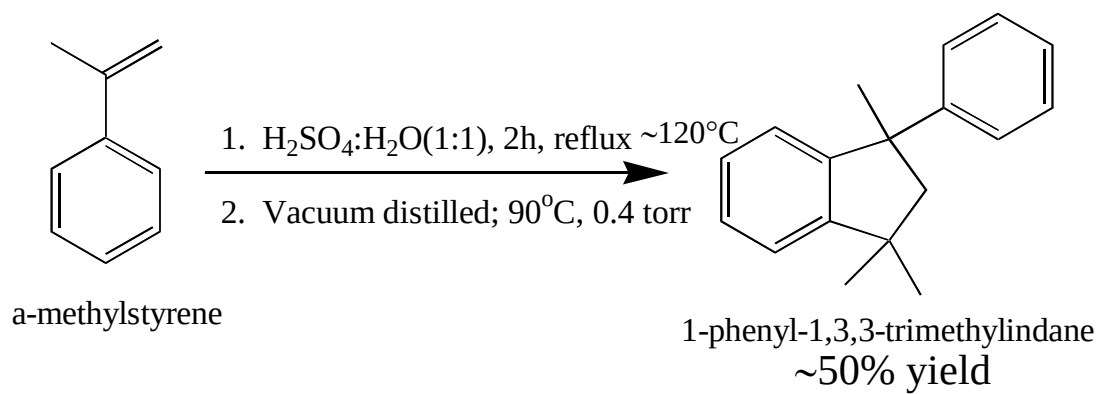
Purification: Used as received

3.2.2 Synthetic Procedure

3.2.2.1 Synthesis of 1-phenyl-1,3,3-trimethylindane (phenylindane)-Scheme 3.2.2.1.1

Following a procedure similar to Maier et al.²⁶⁹

Catechol, a self-polymerization inhibitor, was removed from α -methylstyrene (α -MS) by filtration through basic alumina. Deinhibited α -MS (150ml) was added to a 2L flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet/outlet. To this, a previously mixed acid solution consisting of 480ml H_2SO_4 and 600ml H_2O was added slowly to the α -MS. This mixture was then refluxed ($\sim 120^\circ\text{C}$) for 2 hours, followed by the addition of 300ml H_2SO_4 and continuation of reflux for an additional 18 hours. At this point the reaction mixture was cooled to room temperature and 400ml H_2O was added. The organic layer, which contained the phenylindane, was then washed with 5% NaHCO_3 . The organics containing the phenylindane was then vacuum distilled (90°C , 0.4 torr).



Scheme 3.2.2.1.1 Synthesis of 1-phenyl-1,3,3-trimethylindane from α -methylstyrene

yield=50%. Appearance: white solid, m.p. 50-51°C (lit. 50-52°C); Elemental Analysis: found (expected), C: 90.81 (91.47), H: 8.47 (8.53); NMR assignments, Figures 3.2.2.1.1, 3.2.2.1.2 and 3.2.2.1.3; IR spectra, Figure 3.2.2.1.4.

3.2.2.2 Synthesis of 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (dinitrophenylindane or DNPI) (Scheme 3.2.2.2.1)

Following a procedure similar to Bateman et al.:²⁷⁰

To a 250ml 3-neck flask equipped with a mechanical stirrer and a nitrogen inlet/outlet, 20g of phenylindane was dissolved in 60ml of CHCl_3 . The flask was then placed into an ice bath at 0-5°C. A previously mixed solution containing 33ml H_2SO_4 and 14.5ml HNO_3 (1.95 equivalents) was then added dropwise to the phenylindane/ CHCl_3 over a 2 hour period while maintaining a solution temperature of 0-5°C. The reaction temperature (0-5°C) was maintained for an additional 4 hours before allowing the solution to increase to room temperature. The organic layer was then separated. The acid layer was washed with CHCl_3 , and combined with the organic layer. The organics were neutralized with 5% NaHCO_3 and dried with MgSO_4 . The CHCl_3 was removed from the DNPI using a rotoevaporator, thereby yielding a viscous yellow liquid, which, when triturated in hexane, afforded a light yellow powder. yield=70%. m.p. 110-126°C (lit. 109-125°C); Infrared Analysis: 1343cm^{-1} (NO_2 -assymetric stretch) and 1518cm^{-1} ; Elemental Analysis: found (expected), C: 66.17 (66.25), H: 5.47 (5.56), N: 8.47 (8.58), O: 19.57 (19.61); NMR assignments, Figures 3.2.2.2.1 and 3.2.2.2.2; IR spectra, Figure 3.2.2.1.4.

3.2.2.3 Synthesis of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (diaminophenylindane or DAPI) (Scheme 3.2.2.2.1)

Following a procedure similar to Zhuang's:¹³¹

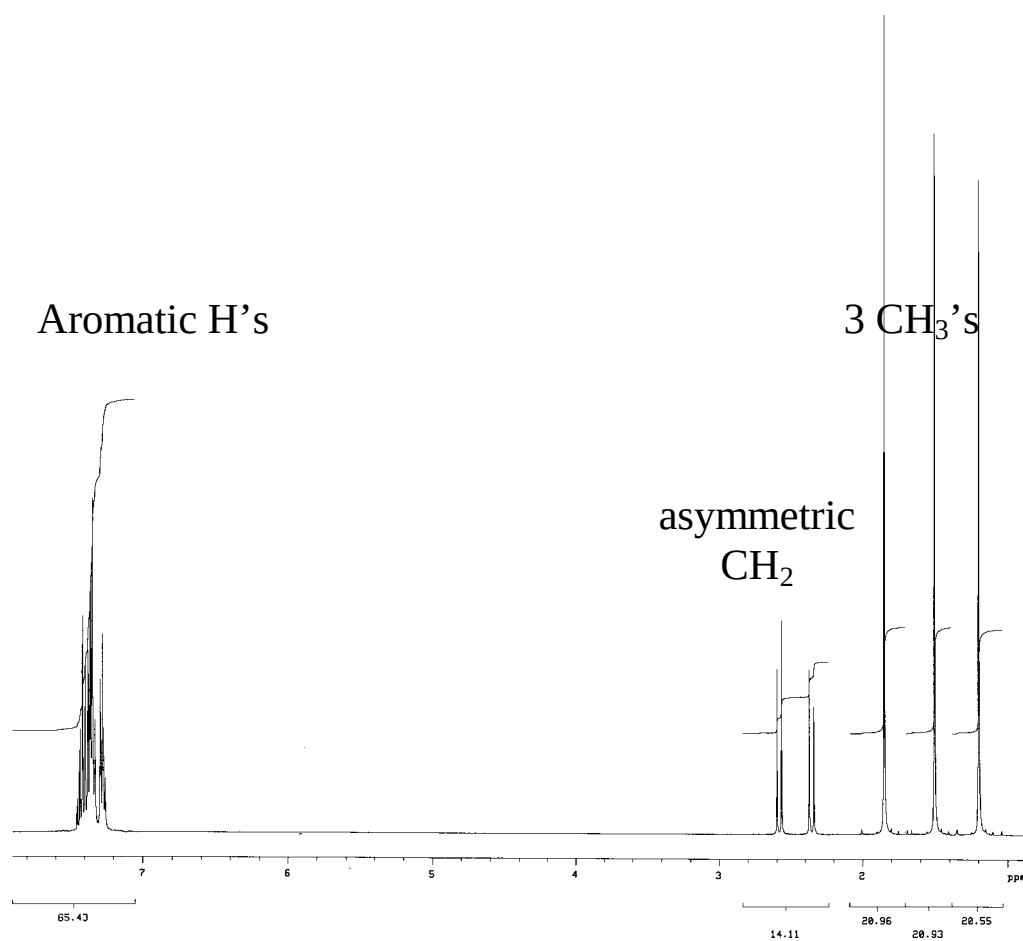
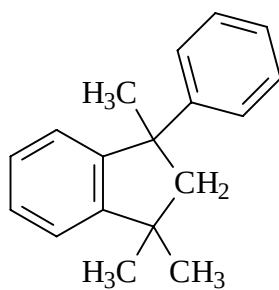


Figure 3.2.2.1.1 ¹H NMR Spectra for 1-phenyl-1,3,3-trimethylindane

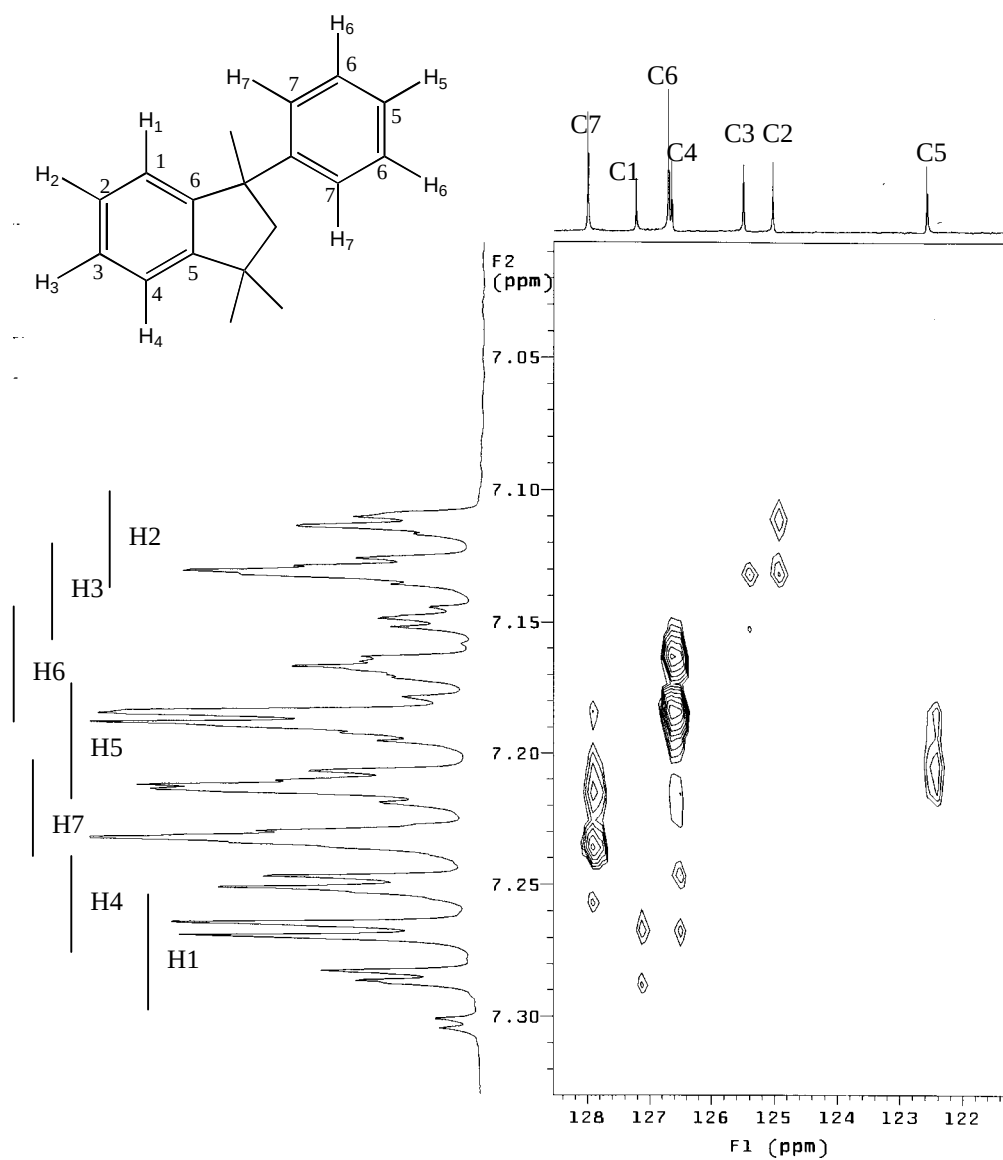


Figure 3.2.2.1.2 HMQC of 1-phenyl-1,3,3-trimethylindane

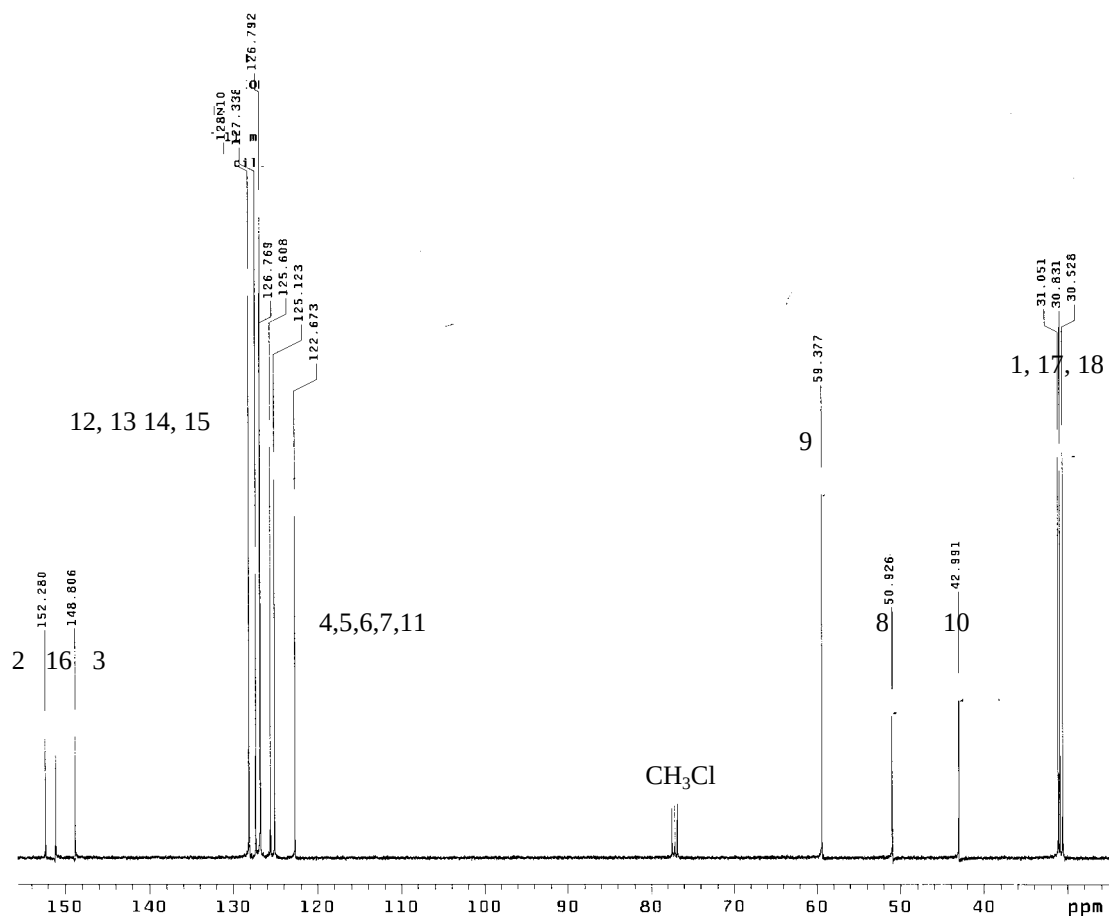
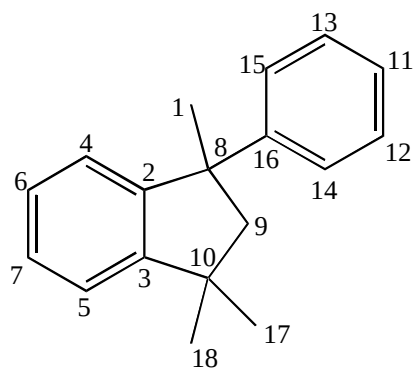


Figure 3.2.2.1.3 ^{13}C NMR of 1-phenyl-1,3,3-trimethylindane

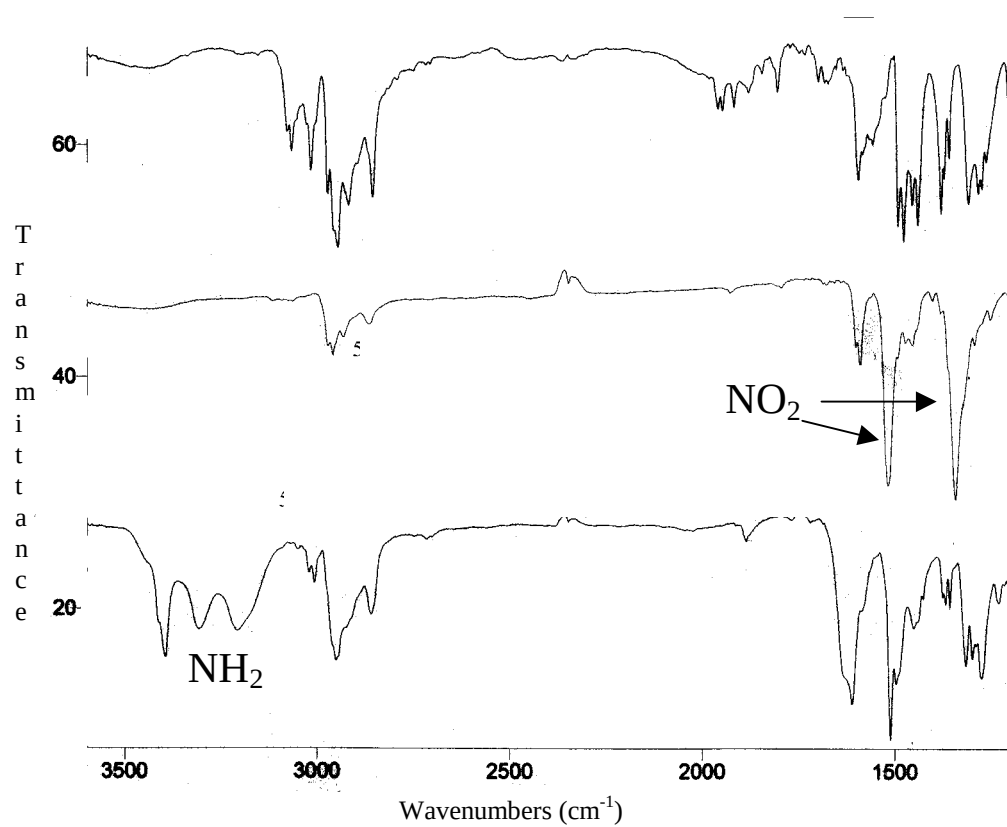
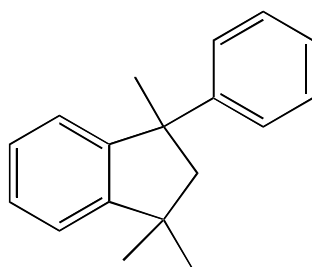
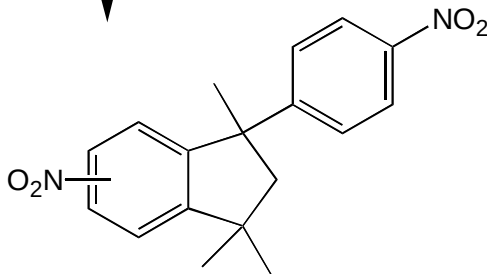


Figure 3.2.2.1.4 IR Spectra (from top to bottom) of 1-phenyl-1,3,3-trimethylindane, 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane and 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane



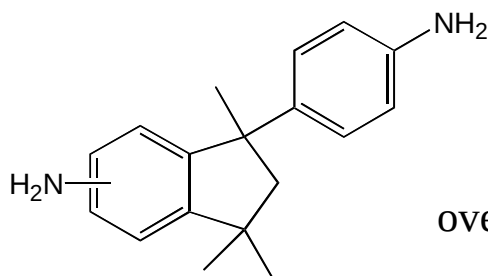
1-phenyl-1,3,3-trimethylindane

1. Dissolution in CHCl_3 (25wt%)
 2. $\text{HNO}_3/\text{H}_2\text{SO}_4$, 0-5°C, 4h
 ($\text{CHCl}_3:\text{H}_2\text{SO}_4/2:1$)



5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

- EtOH at reflux,
 $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ (9X excess),
 Pd/C



overall yield ~35%

5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane

Scheme 3.2.2.2.1 Synthesis of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) from 1-phenyl-1,3,3-trimethylindane

6 & 5 Isomers, 38:62

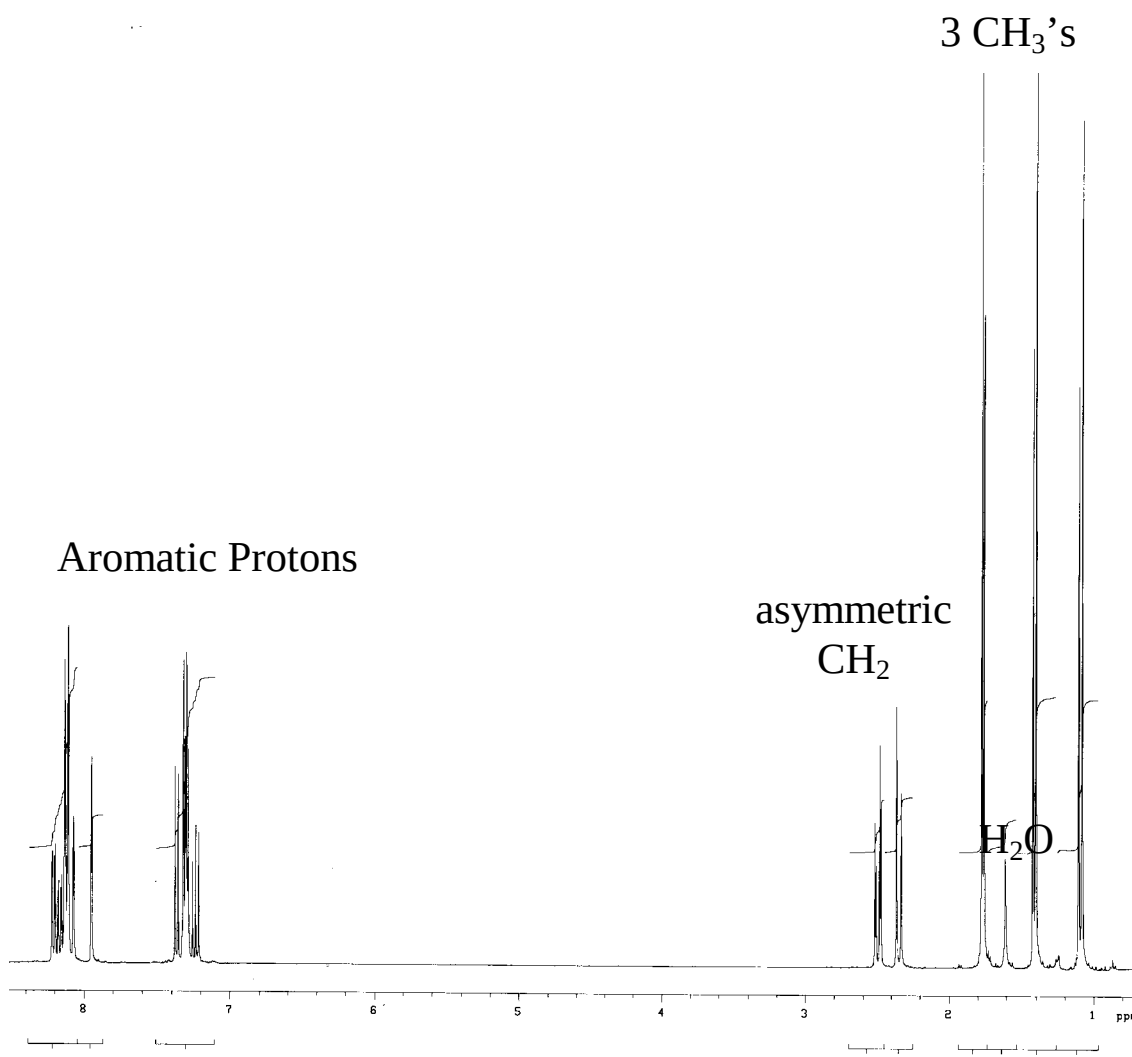
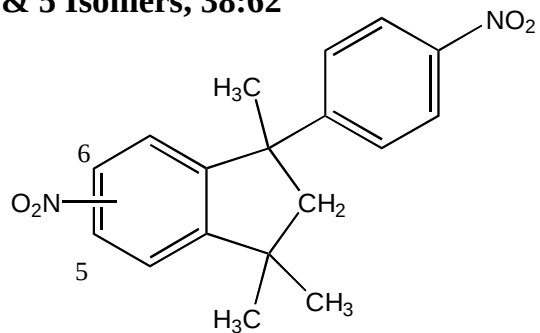


Figure 3.2.2.2.1 ¹H NMR of 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

5&6 Isomers, 38:62

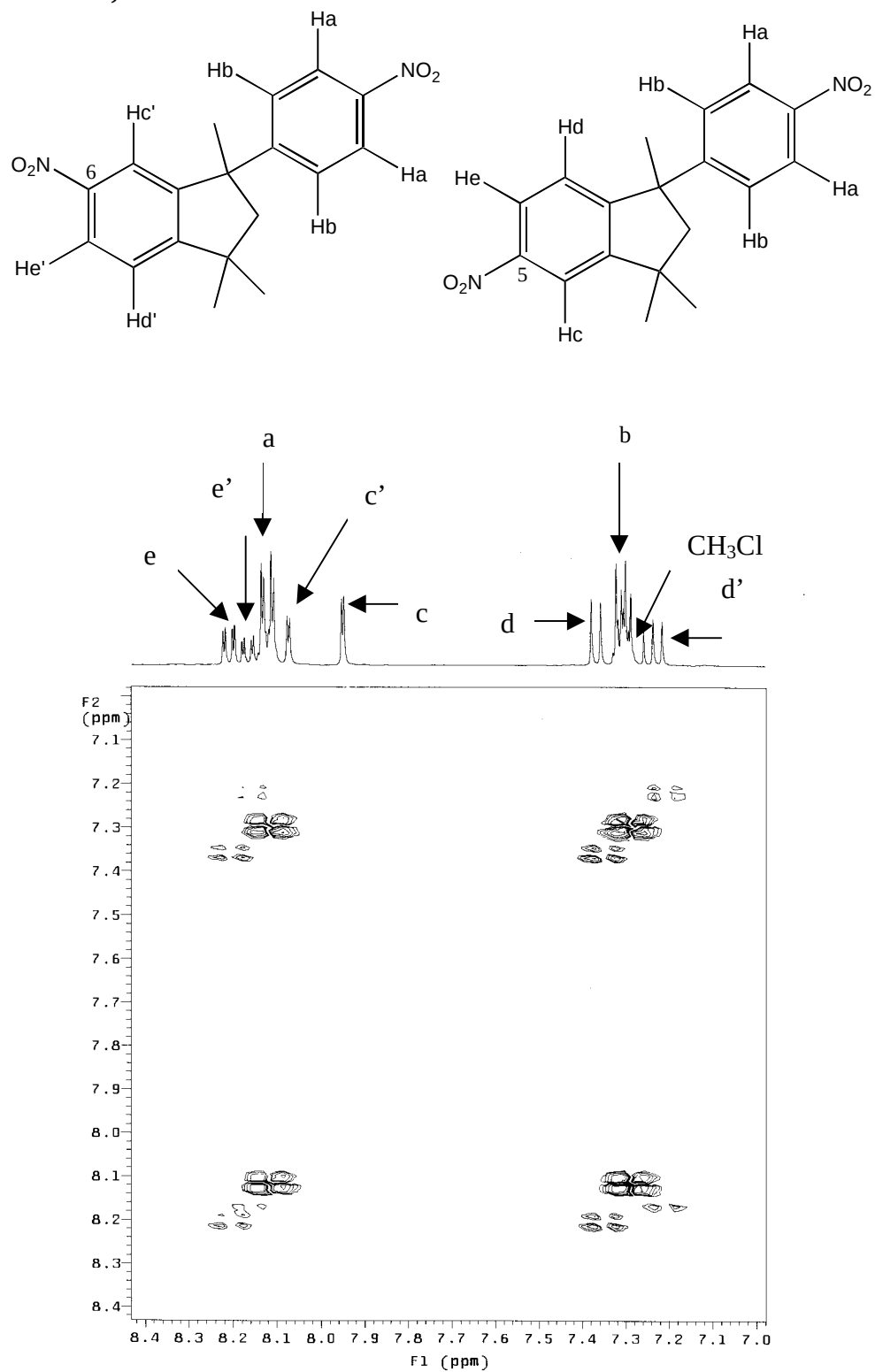


Figure 3.2.2.2.2 DQCosY of 5(6)-nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

To a 3-neck 250ml flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet were added 3g of DNPI and 220ml ethanol and the mixture was heated to reflux. Once dissolved, 0.25g Pd/C was added followed by 12ml of hydrazine (9 molar excess), which was slowly added from a dropping funnel. After the addition, reflux was continued for 2 hours before 0.1g of Pd/C was added. Reflux was continued overnight. Activated charcoal (0.2g) was then added while maintaining reflux. After 10 minutes the reaction mixture was hot filtered through Celite. The ethanol was removed and the resulting oil was triturated in H₂O to afford a white powder. Quantitative yield, m.p. 77-104°C (lit. 47-54°C); Elemental Analysis: found (expected), C: 81.06 (81.16), H: 8.41 (8.32), N: 10.35 (10.52); NMR assignments, Figures 3.2.2.3.1 and 3.2.2.3.2; Infrared Analysis: 1612cm⁻¹ (C-N) and 3207cm⁻¹, 3307cm⁻¹ and 3393cm⁻¹ (N-H stretch) (Figure 3.2.2.1.4)

3.2.2.4 Synthesis of 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (trinitrophenylindane or TNPI) (Scheme 3.2.2.4.1)

To a 250ml 3-neck flask equipped with a mechanical stirrer and a nitrogen inlet/outlet was added 5g of phenylindane dissolved in 40ml of CHCl₃. The solution was then placed into an ice bath at 0-5°C and 30ml of chilled H₂SO₄ solution was added. A previously mixed acidic solution containing 20ml H₂SO₄ and 3.85ml HNO₃ (2 molar equivalents plus 1%) was then added dropwise to the solution over a 20 minute period while maintaining a solution temperature of 0-5°C. Next, the beaker containing the nitric acid was rinsed with 10ml of H₂SO₄. The reaction temperature (0-5°C) was maintained for an additional 4 hours. The acid layer was washed with CHCl₃, which was then combined with the organic layer. The organics were made neutral with 5% NaHCO₃ and dried with MgSO₄. The CHCl₃ was removed from the TNPI using a rotoevaporator yielding a viscous yellow liquid, which when triturated overnight in hexane afforded a light yellow powder. About 3.24g were recovered (50% yield), consisting of a mixture of mono-, di- and tri-substituted product. The tri-substituted isomer was readily

6 & 5 Isomers, 43:57

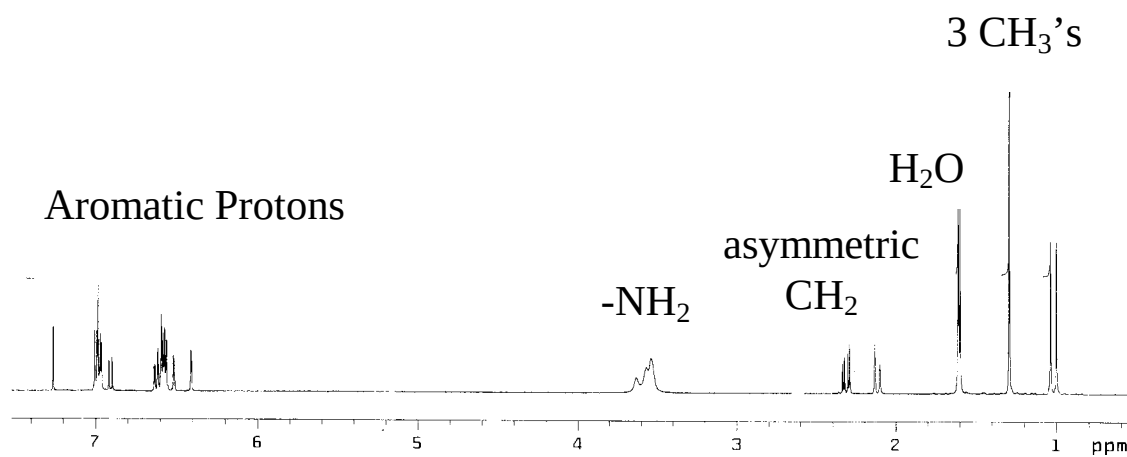
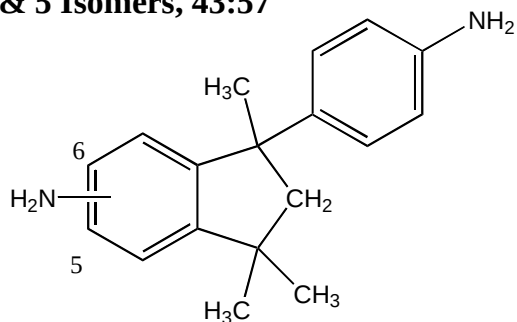


Figure 3.2.2.3.1 ^1H NMR of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane

5&6 Isomers, 43:57

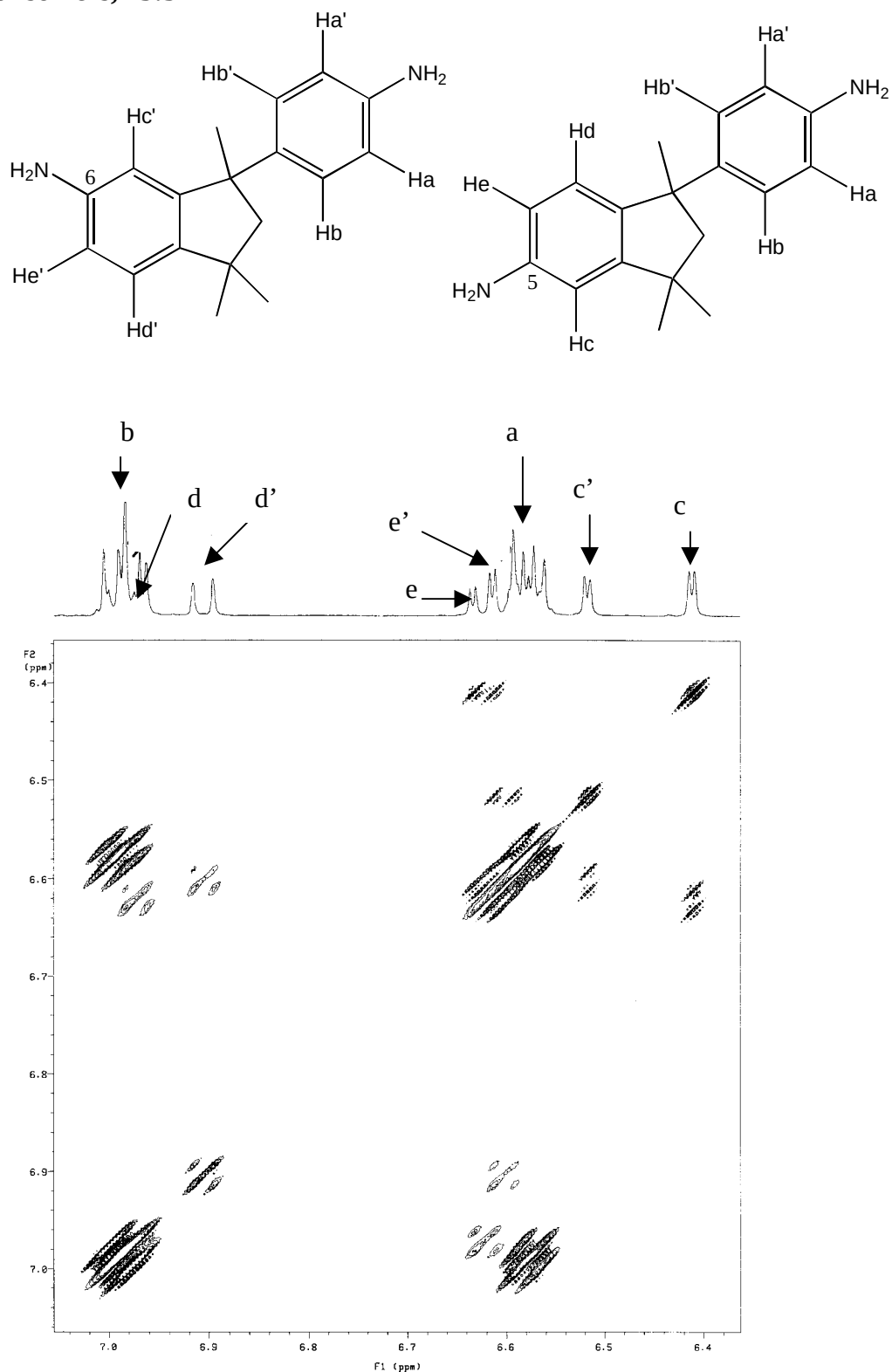
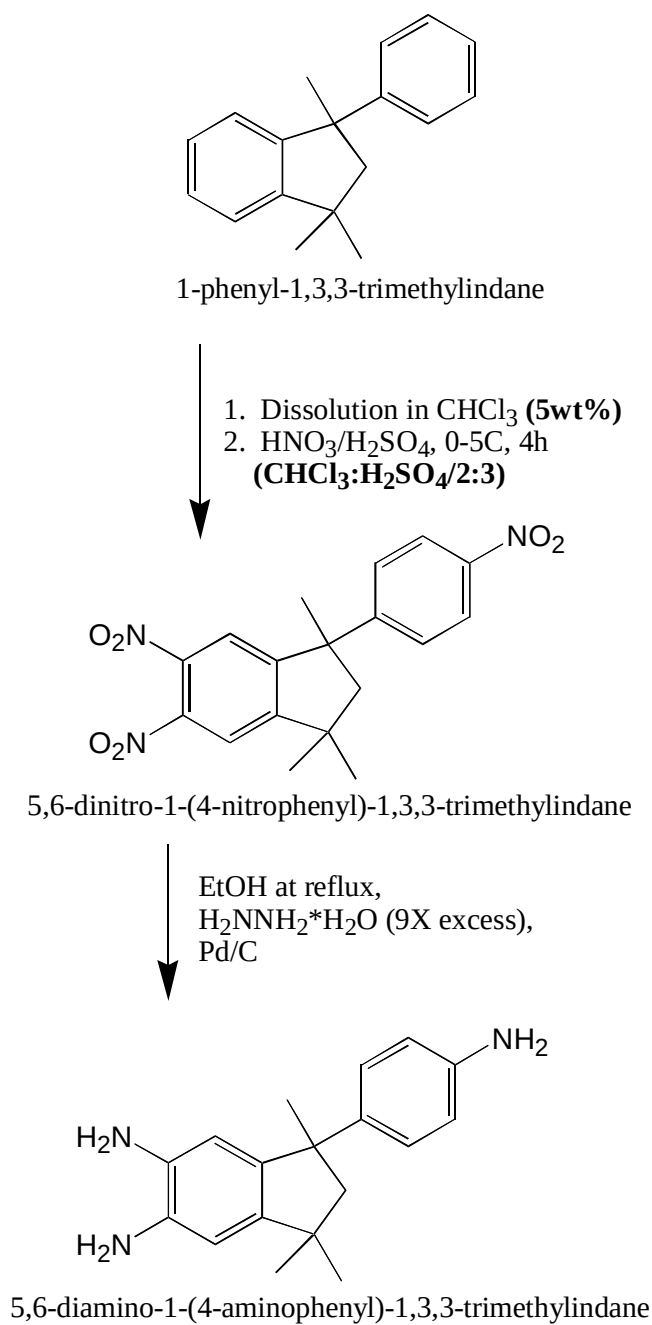


Figure 3.2.2.3.2 DQCoSY of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane



Scheme 3.2.2.4.1 Synthesis of 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane (TAPI) from 1-phenyl-1,3,3-trimethylindane

recrystallized from ethanol to afford a crystalline yellow powder. m.p. 184-185°C (new compound); Elemental Analysis: found (expected), C: 57.98 (58.22), H: 4.66 (4.61), N: 11.11 (11.32), O: 25.98 (25.85); NMR assignments, Figures 3.2.2.4.1 and 3.2.2.4.2.

3.2.2.5 Synthesis of 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane (triaminophenylindane or TAPI) (Scheme 3.2.2.4.1)

To a 3-neck 500ml flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet were added 3.85g of TNPI and 375ml ethanol, which was subsequently heated to reflux. Once dissolved, 0.15g Pd/C was added followed by 16ml hydrazine (9 molar excess), which was slowly added from a dropping funnel. After the addition, reflux was continued for 4 hours before 0.1g of Pd/C was added and refluxed overnight. Activated charcoal (0.2g) was then added while maintaining reflux. After 10 minutes the hot reaction mixture was filtered through Celite. The ethanol was removed and the resulting oil was triturated in H₂O to afford a light gray powder. yield~95%. m.p. 140-142°C (new compound); Elemental Analysis: found (expected), C: 76.23 (76.83), H: 8.15 (8.24), N: 14.89 (14.93); NMR assignments, Figure 3.2.2.5.1.

3.2.2.6 Synthesis of 4-hydroxy- α -methylstyrene (isopropenylphenol or IPP) (Scheme 3.2.2.6.1)²⁷²

To a 500ml 3-neck round bottom flask equipped with a mechanical stirrer (with vacuum adapter) and a vacuum fixture with a collection flask (Figure 3.2.2.6.1) was added 250g bisphenol A and 0.87g NaOH (~0.35wt%). The reaction flask was heated under vacuum at 175°C until most of the solids had melted (bisphenol A, m.p. 156°C). The reaction temperature was increased to 220°C, while maintaining a reduced pressure of ~350mmHg, for 2 hours. This was followed by increasing the temperature to 250°C for 6 hours under a pressure of ~50mmHg. At this point, during the period of several hours, a yellow solid was observed to distill over at 125-145°C. The yield of the yellow

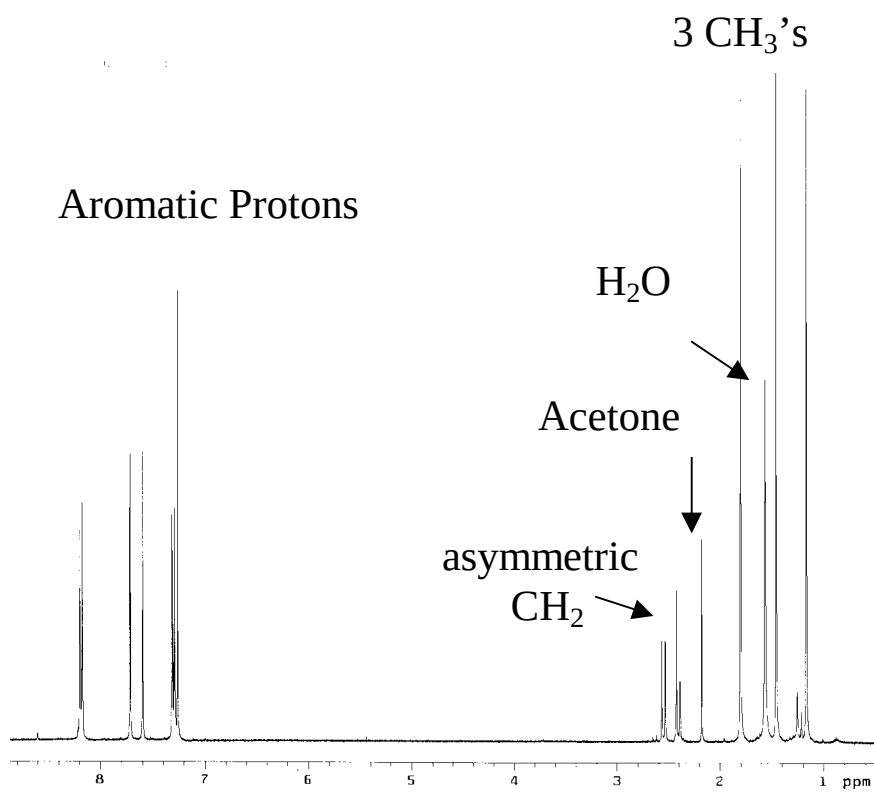
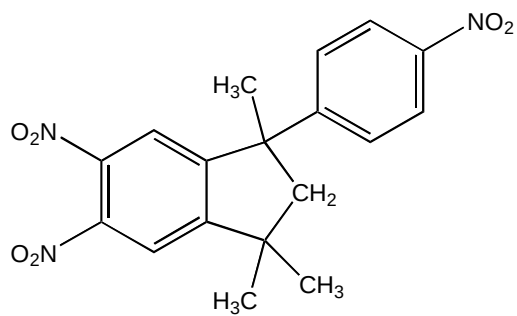


Figure 3.2.2.4.1 ^1H NMR of 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

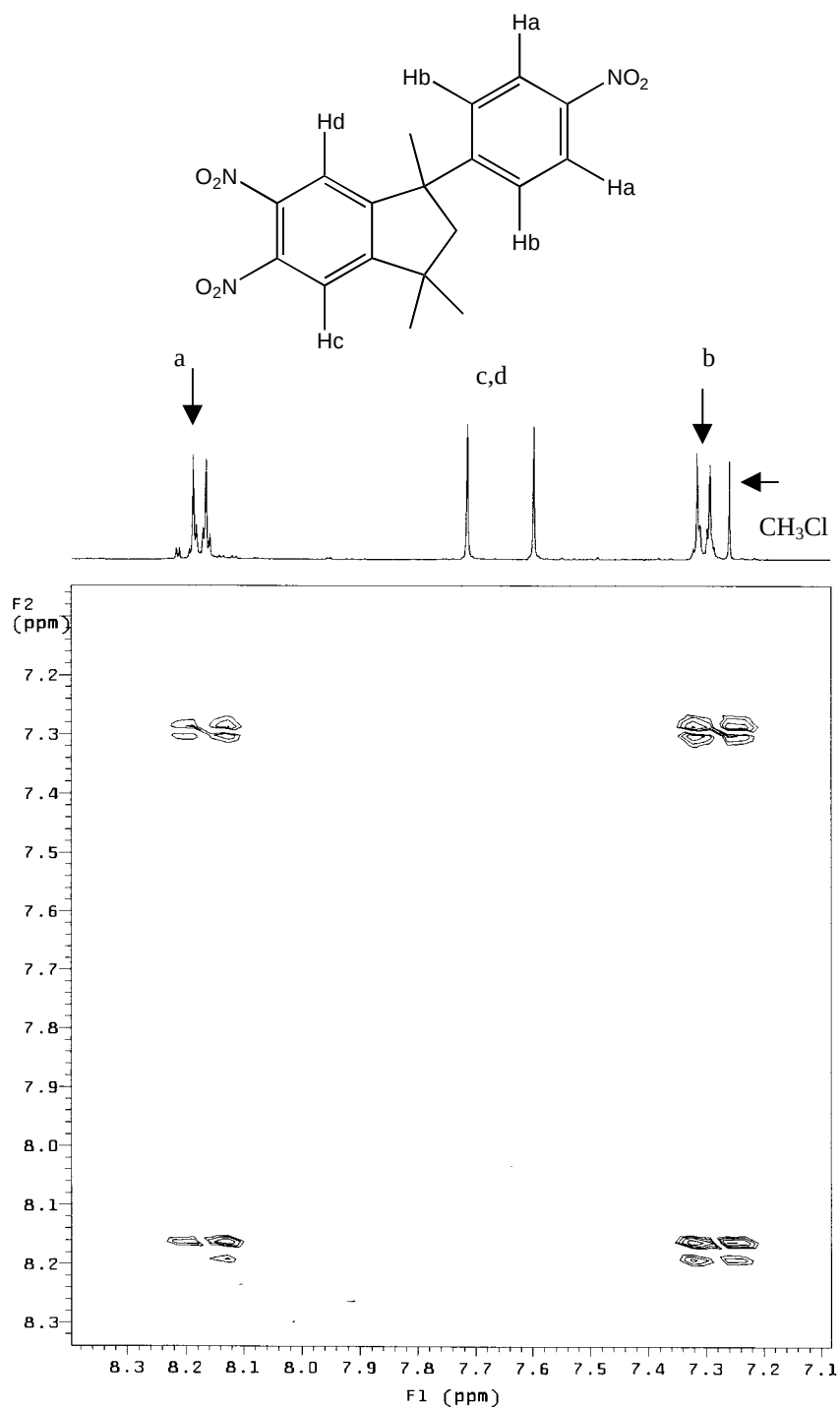


Figure 3.2.2.4.2 DQCosY of 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane

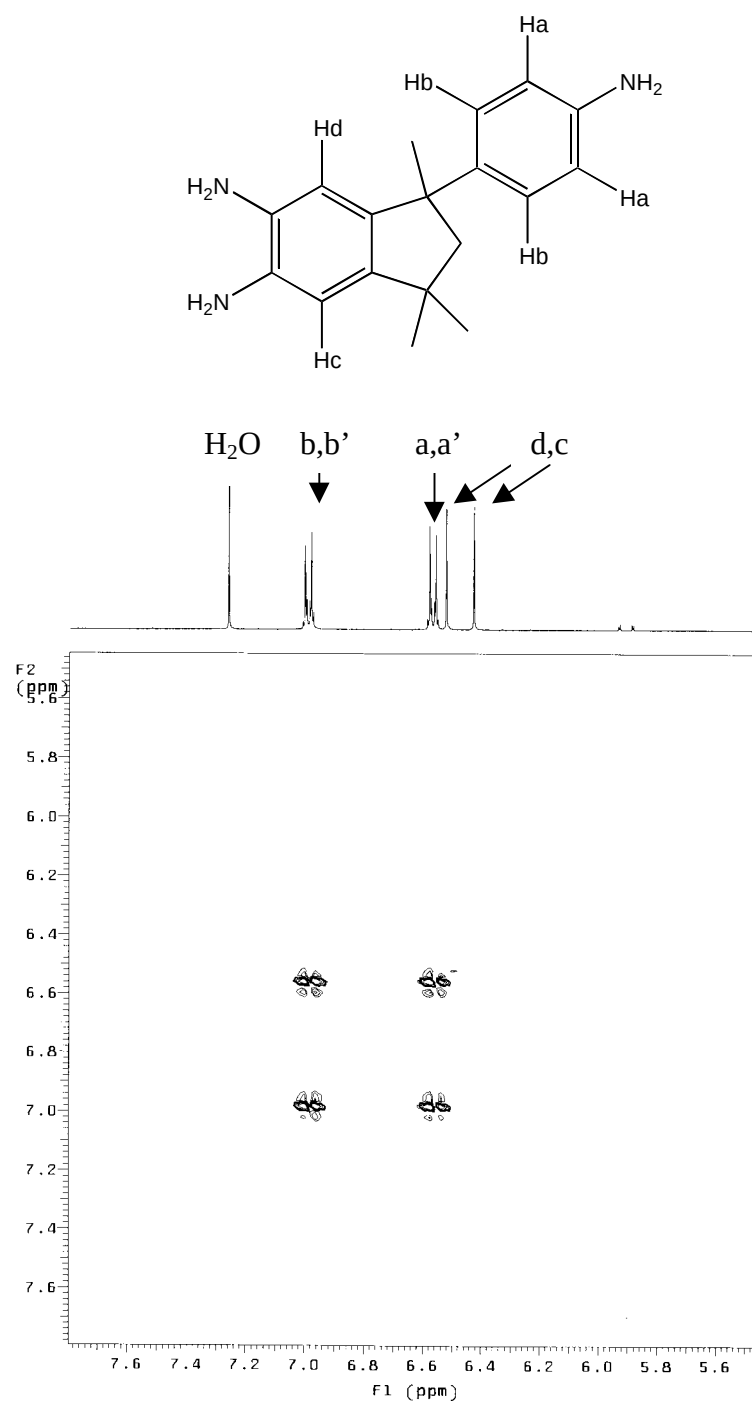
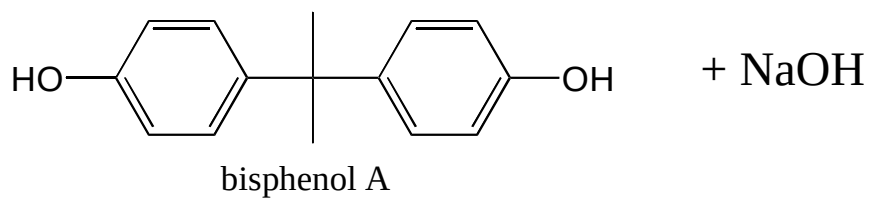
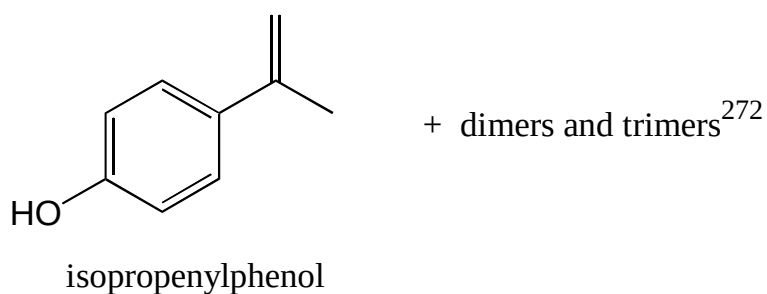


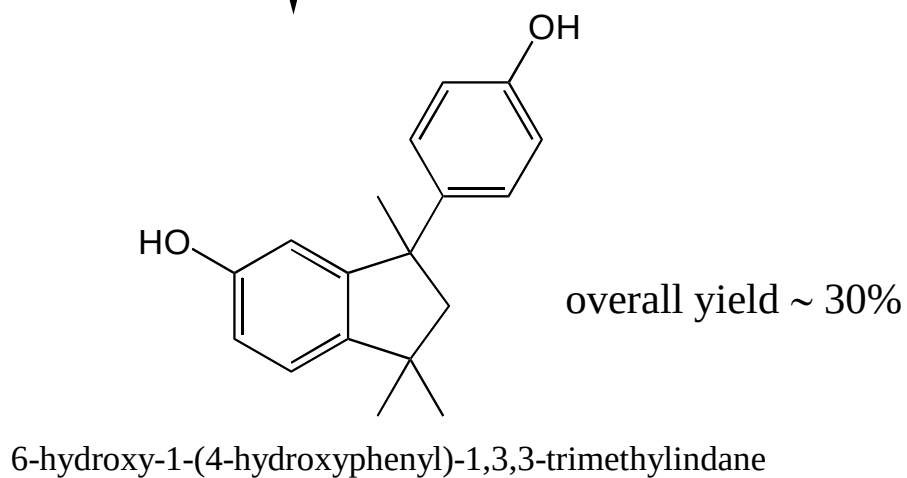
Figure 3.2.2.5.1 DQCOSY of 5,6-diamino-1-(4-aminophenyl)-1,3,3-trimethylindane



- ↓ 1. 175C until melt
 220C, 2h, 350mmHg
 250C, 6h, 50mmHg
 2. PhOH removed by distillation



Trifluoroacetic Acid, R.T., 24 hours



Scheme 3.2.2.6.1 Synthesis of 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI)

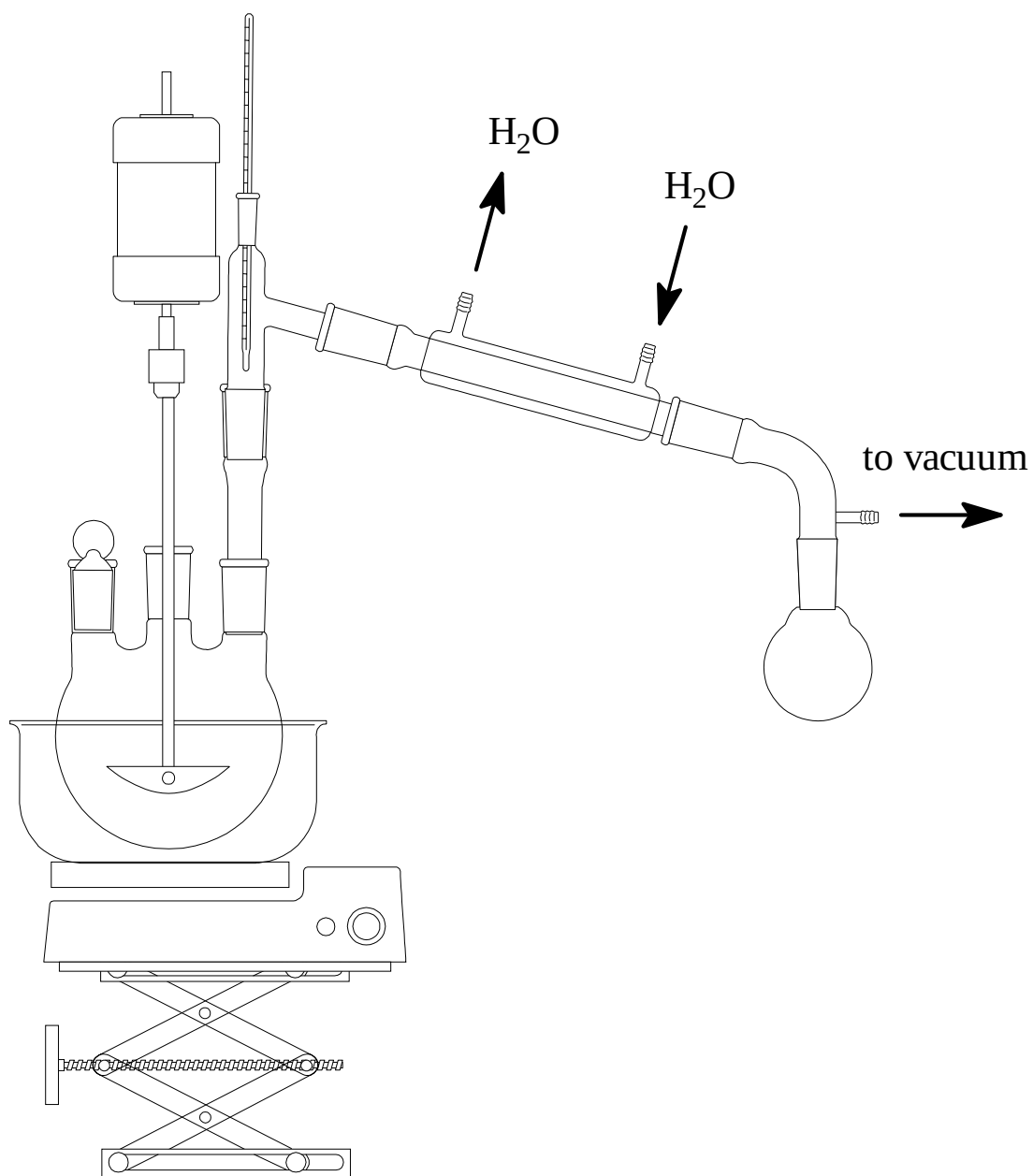


Figure 3.2.2.6.1 Reaction Apparatus for the Synthesis of 4-hydroxy- α -methylstyrene

solid was 180g, which was surmised to consist of phenol and isopropenylphenol (IPP).²⁷² To a 500ml flask, equipped as shown in Figure 3.2.2.6.1, 180g of the phenol/IPP mixture was added. Phenol (identified as such by ¹H NMR and its melting point) was removed at 90-140°C under a reduced pressure of 5 torr. Throughout this distillation the mixture became increasingly more viscous due to the removal of a low molecular weight molecule (phenol) and, more than likely, oligomerization of IPP. The resulting yellow oil was recovered in a 56g quantity and solidified at room temperature.

3.2.2.7 Synthesis of 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (dihydroxyphenylindane or DHPI) (Scheme 3.2.2.6.1)

Following a procedure similar to Dai's:²⁷¹

To a 500ml 3-neck flask equipped with a mechanical stirrer and a condenser were charged 56g of a mixture of IPP and IPP dimers and trimers. (Note: At room temperature the mixture is a solid. Therefore, immediately after the removal of phenol in the previous step, it was transferred while hot to the 3-neck reaction flask). To the reaction flask containing the mixture of IPP structures were slowly added ~150ml trifluoroacetic acid. This reaction mixture was held at room temperature for 24 hours. Trifluoroacetic acid (b.p. 72°C/760mmHg) was then removed under vacuum to yield a dark red, viscous solution. Once dissolved in ether, the solution was washed with 5% NaHCO₃. Upon removal of the ether, the viscous residue was dissolved in toluene and triturated in hexane affording a light gray powder. Recovered yield, 41.1g (~30%). m.p. 193.5-195°C (lit. 194-195°C); Elemental analysis: found (expected); C:80.56 (80.23), H:7.51 (7.51); NMR Assignments, Figures 3.2.2.7.1 and 3.2.2.7.2.

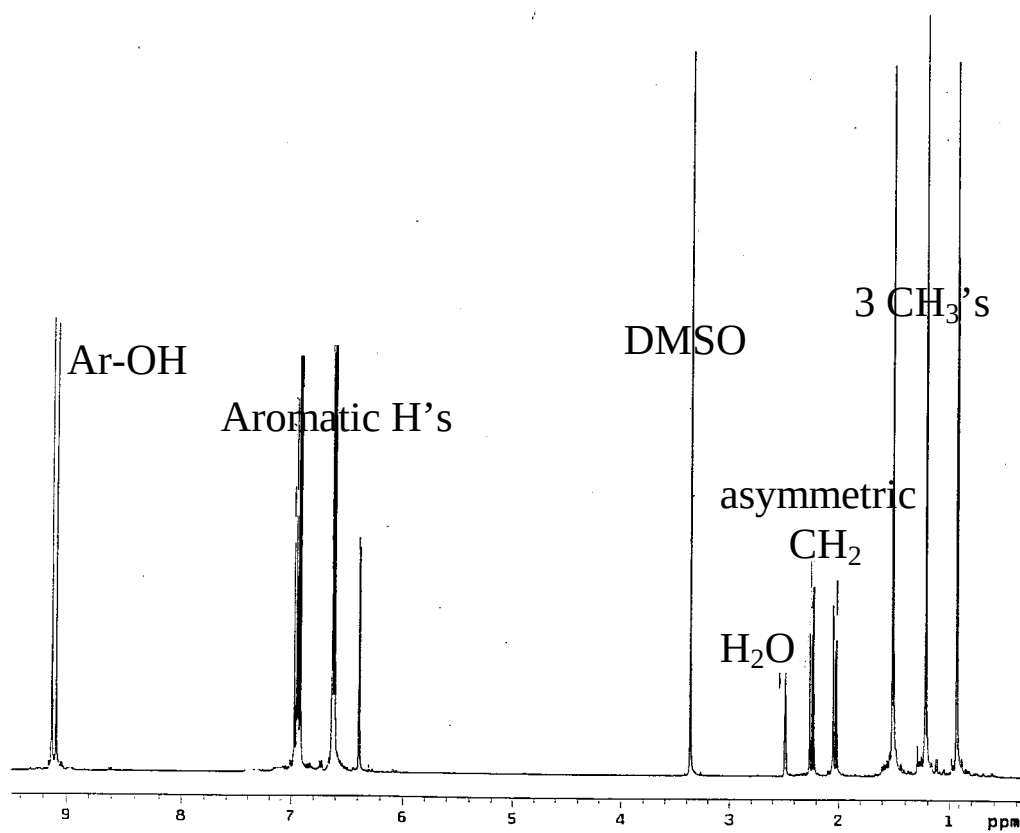
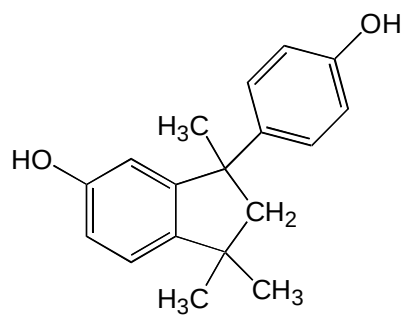


Figure 3.2.2.7.1 ^1H NMR of 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane

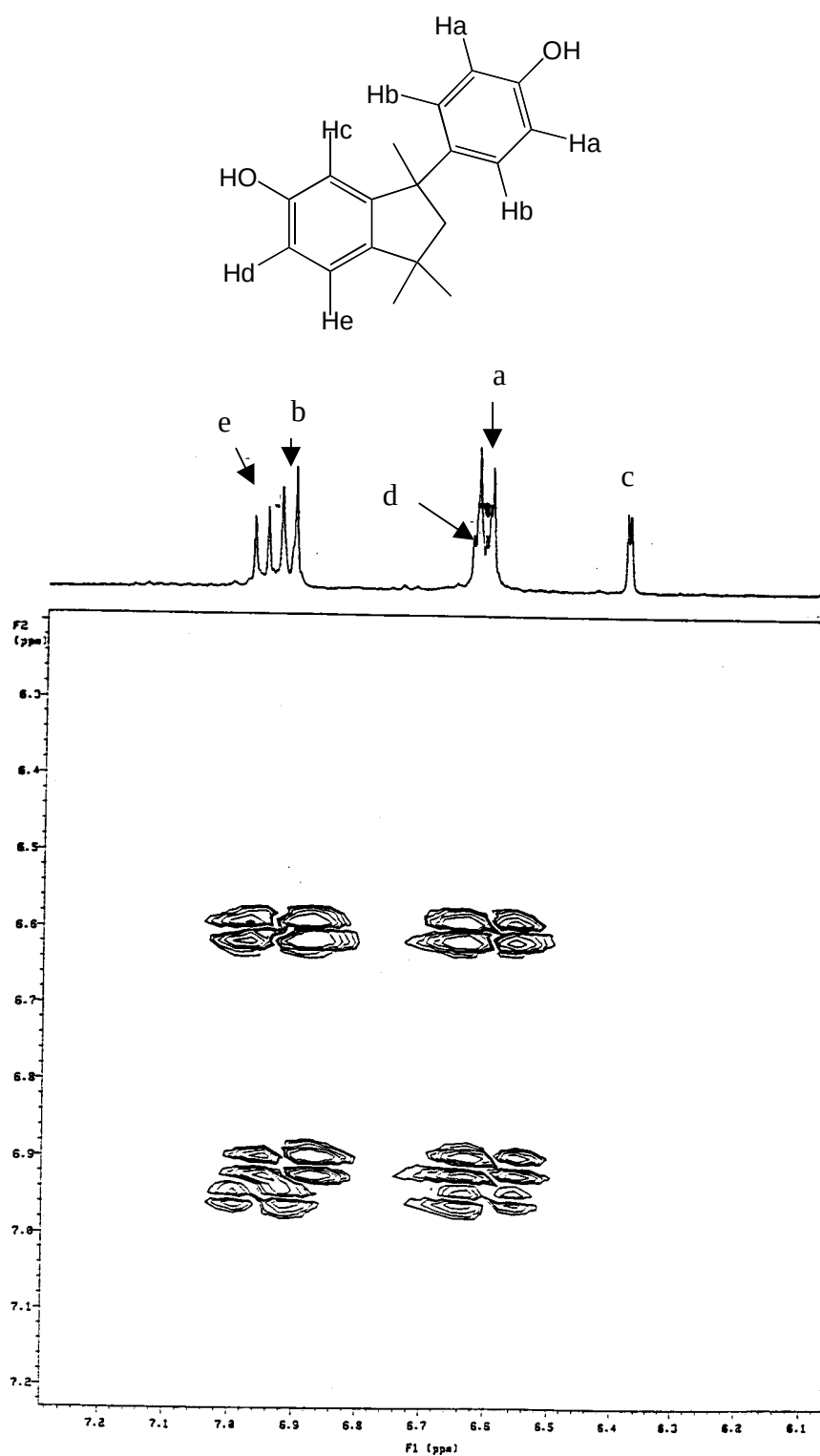


Figure 3.2.2.7.2 DQCosY of 6-hydroxy-(4-hydroxyphenyl)-1,3,3-trimethylindane

3.3 Characterization Methods

3.3.1 Intrinsic Viscosity (IV)

Intrinsic viscosity measurements provided a qualitative measurement of molecular weight. Measurements were conducted using a Cannon-Ubbelohde viscometer at $25\pm 1^\circ\text{C}$ with NMP as the solvent. The reported values result from the linear extrapolation of four different sample concentrations to zero concentration.

3.3.2 Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC)

GPC was conducted with a Waters GPC/ALC 150C chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. Waters μ Styragel HT3 + HT4 columns were used. The mobile phase was NMP, containing 0.02M P_2O_5 . The flow rate was 1.0 mL/min, the injection volume was 200 μL ; the experimental temperature was 60°C ; the polymer concentration was approximately 4 mg/mL. TriSEC GPC Software V2.70e (Viscotek) was used to acquire and analyze the data. A series of polystyrene standards having narrow molecular weight distributions (Polymer Laboratory) were employed to generate the universal calibration curve.^{87,88}

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to confirm functional groups within both the monomers and polymers. Measurements were conducted on a Nicolet Impact 400 FTIR Spectrometer using either KBr pellets containing 1-5 wt% of monomer, or on thin polymeric films.

3.3.4 Polymer Solubility

Polyimide solubility was determined at targeted concentrations of 10% (w/v) in a number of solvents including methylene chloride, chloroform, THF, NMP and DMAc. “Soluble” polyimides went into solution at room temperature, whereas “insoluble” polyimides precipitated out of solution after being cooled from a soluble state at higher temperatures. Visibly swollen polyimides were designated as “swelled” and partially soluble systems as “slightly swelled”.

3.3.5 Thermogravimetric Analysis (TGA)

Dynamic TGA was employed to assess weight loss and thermal stability of polyimide samples using a Perkin Elmer TGA-7 Thermogravimetric Analyzer. Prior to this experiment the samples were carefully dried to remove possible solvent contribution to the reported 5% weight loss values. The typical heating rate was 10°C/minute in either nitrogen or air. Estimated error: $\pm 10\text{wt}\%$

3.3.6 Differential Scanning Calorimetry (DSC)

DSC provided information on polymer thermal transitions. Glass transition temperatures (T_g) reported were obtained on a Perkin Elmer DSC-7 Differential Scanning Calorimeter. Scans were conducted under nitrogen at a heating rate of 10°C/min, unless otherwise stated. Second heat T_g values are reported as the midpoint of the change in slope of the baseline. Estimated error: $\pm 3^\circ\text{C}$

3.3.7 Water Sorption

Water uptake was determined on polyimide thin films dried to constant weight at 200°C and then immersed in either water at 30°C, or 50% humidity at 25°C. The films were then monitored periodically until a constant weight percent of water uptake was found.

3.3.8 Polyimide Oligomer and Epoxy Resin Titrations

Non-aqueous potentiometric titrations were employed to determine the molecular weight of amine terminated polyimides and the epoxy equivalent weight (EEW) of epoxy resins using a MCI GTOS Automatic Titrator equipped with a standard calomel electrode and reference electrode.

A typical amine terminated polyimide titration was conducted as follows:

Hydrogen bromide in acetic acid was the titrant for oligomeric amine terminated polyimides. The titrant ($\sim 0.02N$) was standardized with dry potassium hydrogen phthalate (KHP) immediately prior to titrating. The polymer was completely dissolved in a solvent mixture of chloroform:acetic acid (5:1, v/v) before conducting the experiment. The end-point was detected as the maximum of the first derivative for the potential versus volume of titrant used. The end-point was then used to calculate the number of reactive groups in the system. The calculated number average molecular weight values were very reproducible, $\pm 1.0\%$ (typically 3-5 runs).

A typical epoxy resin titration was conducted as follows:

Perchloric acid with a phase transfer agent, tetramethylammonium bromide, was utilized for the titration of epoxy resins. The titrant ($\sim 0.02N$) was standardized with dry potassium hydrogen phthalate (KHP) immediately prior to titrating. The epoxy resin was completely dissolved in chloroform before conducting the experiment. The end-point was detected as the maximum of the first derivative for the potential versus volume of titrant used. The end-point was then used to calculate the epoxy equivalent weight (EEW), which is the number of grams of epoxy resin per mole of reactive epoxide rings. The calculated EEW values were very reproducible, $\pm 1.0\%$ (typically 3-5 runs).

3.3.9 Refractive Index (RI) Measurement

Refractive indices of thin polymer films were measured on a Metricon™ Model 2010 prism coupler thin film thickness/refractive index measurement system (633nm),

with an index accuracy of ± 0.001 , and an index resolution of ± 0.0005 . Prism type: 200-P-4.

3.3.10 Permeation Apparatus

The homopolyimides used in this study were in the form of dense, planar (sheet) membranes varying in the thickness from 15-40 μm . Films were solution cast from NMP and dried under vacuum at 200°C for 24 hours. The solvent-free thin films were immediately used in the gas permeation device to avoid moisture uptake.

Measurement of the permeability coefficients were performed at Medall by Mr. Dean Kratzner. Figure 3.3.10.1 shows the apparatus used in this experiment. The O_2 and N_2 permeabilities of polymer membranes were characterized at 30°C by a mean permeability coefficient with units of barrer (Ba).

$$1 \text{ Ba} = 10^{-10} \text{ cm (STP)/(cm}^2\text{*sec*cmHg)}$$

The experimental procedure was as follows:

The membrane was mounted in a permeation cell prior to degassing the whole apparatus. Permeant gas was then introduced on the upstream side, and the permeant pressure on the downstream side was monitored using a MKS-Baratron pressure transducer. From the known steady-state permeation rate, pressure difference across the membrane, permeable area and film thickness, the permeability coefficient was determined.

3.3.11 Melting Point (m.p.) Measurement

A Lab Devices Melt-Temp II was used to determine melting points of purified compounds. Heating rate $< 1^\circ/\text{min}$.

3.3.12 High Performance Liquid Chromatography (HPLC)

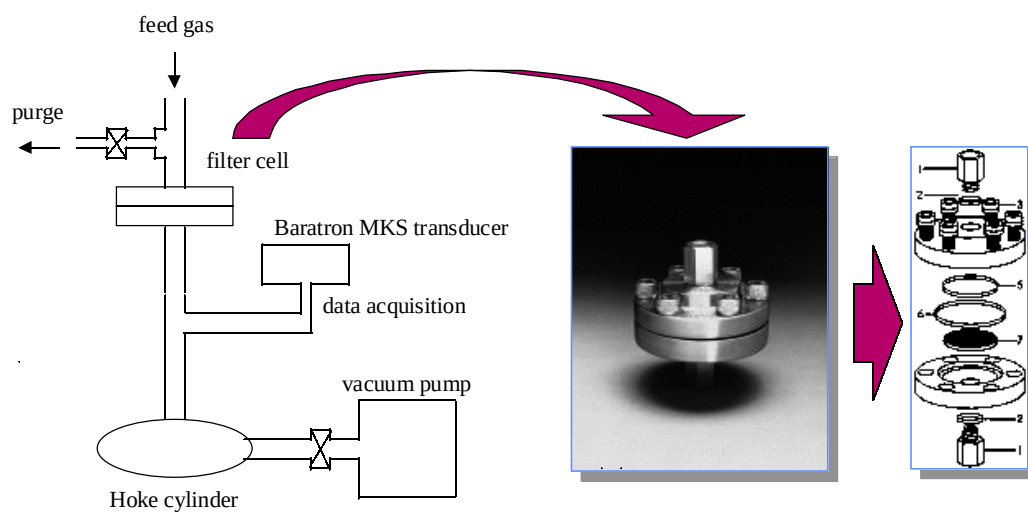


Figure 3.3.10.1 Gas Permeation Apparatus

Reversed-phase high performance liquid chromatography (HPLC) analyses were conducted on a Vista 5500 with an C-18 (octadecyl or ODS) column. Separation of the two DAPI isomers required an initial mobile phase composition of 50% acetonitrile/50% water. After 5 minutes, the schedule allowed for a gradient change to 100% acetonitrile over 20 minutes. Rate 1ml/min, UV detector (254nm).

3.3.13 Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear magnetic resonance (^1H and ^{13}C) spectra were obtained using a Varian Unity 400 Spectrometer. NMR was used primarily to determine monomer purity and to confirm molecular structure of newly synthesized monomers.

3.4 Polymerization Methods

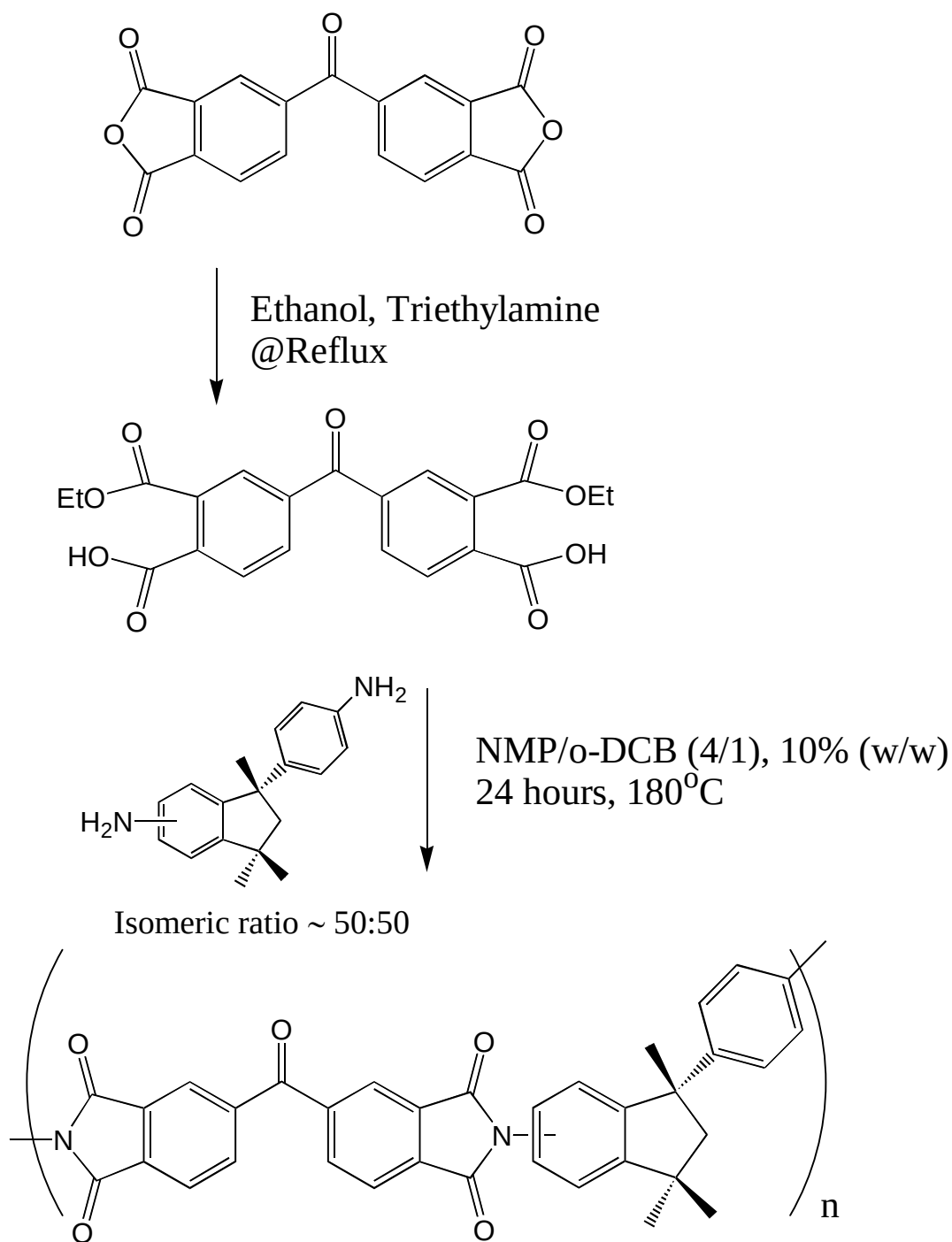
Four synthetic procedures were utilized to form high molecular weight polyimides. These were: chemical, high temperature solution, thermal and ester-acid precursor imidization. In the following sections, typical procedures are given for each of these methods.

3.4.1 Ester-Acid Precursor Method for the Formation of High Molecular Weight 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione (6FDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

A general scheme for all of the polymers synthesized by this method is shown in Scheme 3.4.1.1.

A typical example is as follows. To a three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a reverse Dean-Stark trap with a condenser (Figure 3.4.1.1), 2.500 g (5.63×10^{-3} mol) of 6FDA was charged and rinsed in with 40ml of ethanol and 3ml triethylamine. Under refluxing conditions, the ethyl ester-acid of the dianhydride was formed. After approximately one hour, the excess ethanol and triethylamine had distilled into the trap leaving a viscous ester-acid mixture. The diamine, DAPI, was added to this mixture in an equimolar amount, 1.4997 g (5.63×10^{-3} mol), and washed in with NMP/*o*-DCB (4/1) to give ten weight percent solids. The trap was drained and filled with the azeotroping solvent, *o*-DCB. The solution temperature was then raised to 180°C to obtain fully cyclized imide linkages.²¹ Within a few minutes, distillation of ethanol and water were observed as the amic acid was formed, followed quickly by imidization.

The viscous solution was cooled after 24 hours of reaction time and precipitated into stirred methanol. The polymer solids were filtered and washed with methanol and diethylether. The resulting powder was dried under vacuum at 180°C for 24 hours.



Scheme 3.4.1.1 Ester-Acid Precursor Method for the Formation of High Molecular Weight 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione (6FDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

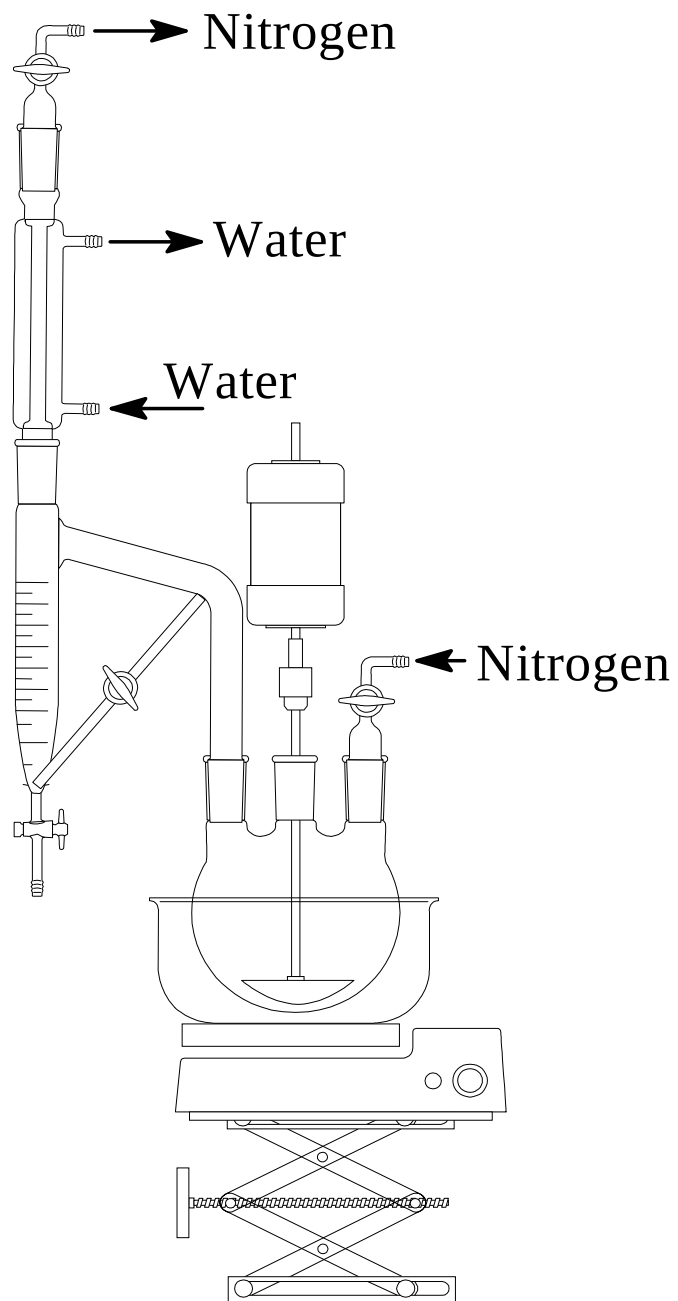


Figure 3.4.1.1 Polymerization Apparatus

3.4.2 Chemical Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

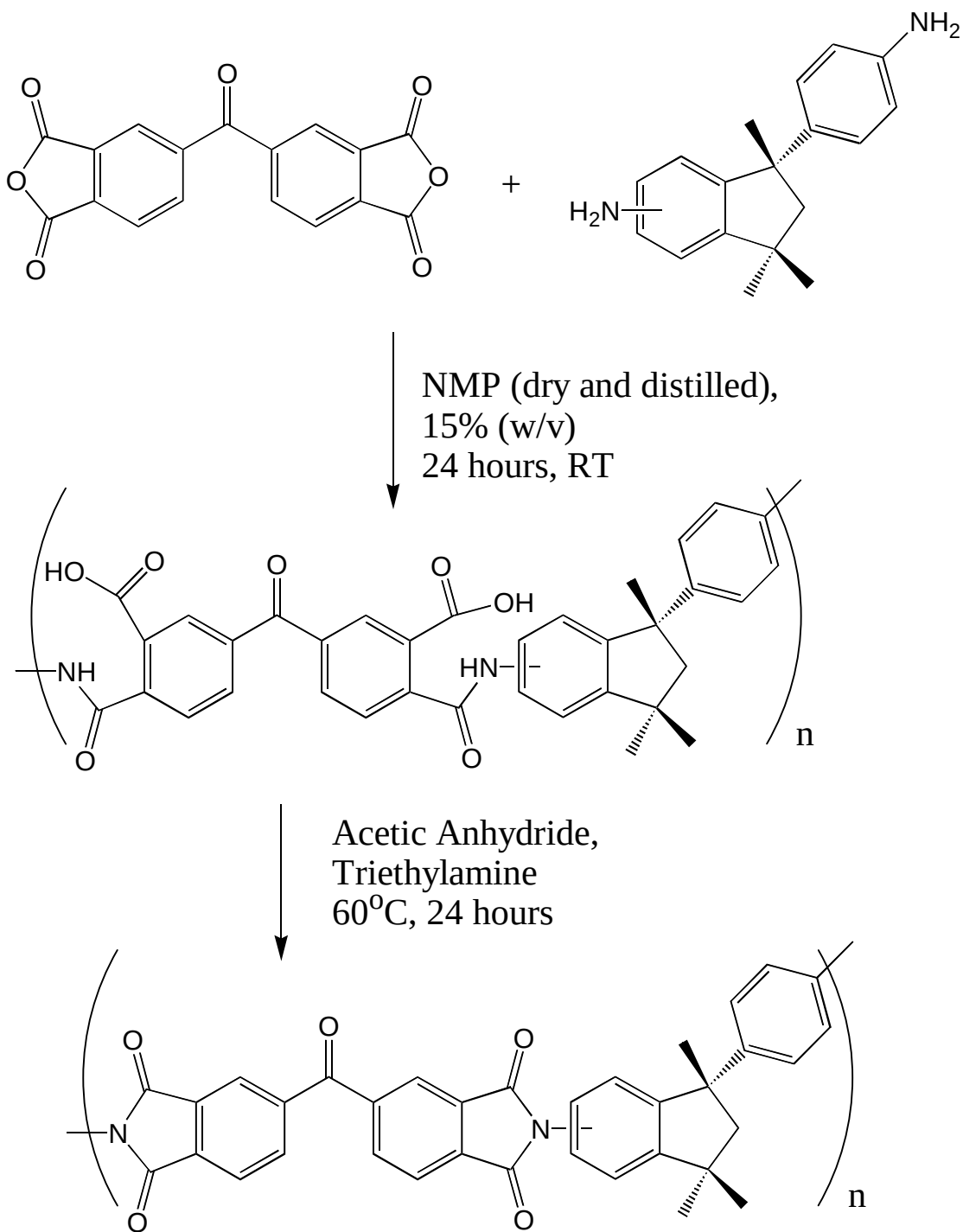
A general scheme for polyimides synthesized by the chemical imidization method is shown in Scheme 3.4.2.1.

A typical example is as follows. To a flame dried three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a condenser (Figure 3.4.1.1), 2.1311g (8 mmol) of DAPI was added followed by 15 ml of dried and distilled NMP. Once dissolved, 2.5778g (8 mmol) of BTDA was slowly added over a 30 minute period. The purpose of slowly adding the dianhydride to the diamine was to favor the reaction of the anhydride moieties with the excess amine versus hydrolysis of anhydride by residual water. The BTDA was rinsed in with 16.4ml of NMP to give a total weight percent of 15% (w/v). The solution was stirred for 24 hours at room temperature to form the polyamic acid of DAPI and BTDA.

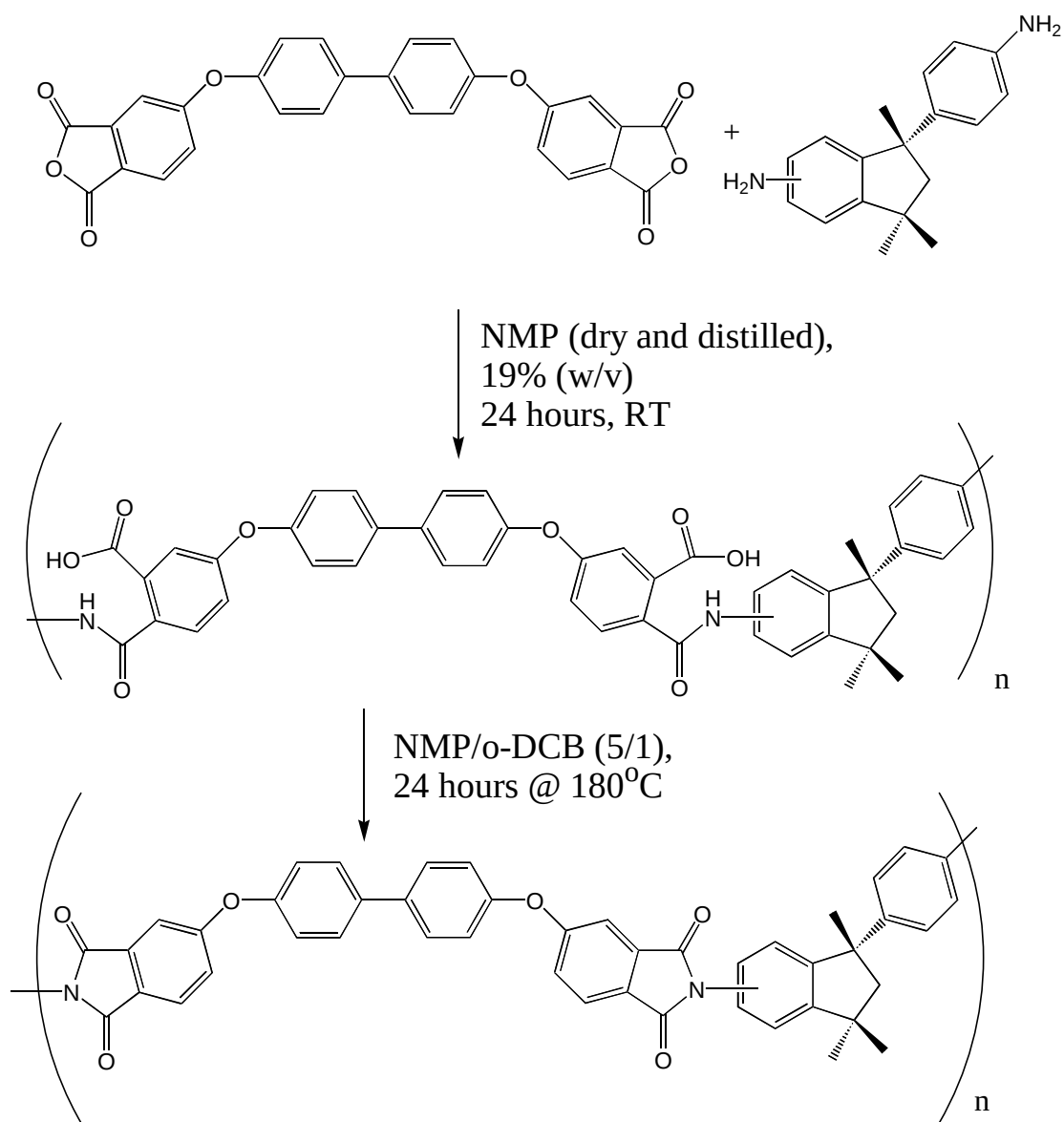
To cyclize the polyamic acid to the polyimide, 4.9ml (6 molar excess) of acetic anhydride and 4.9ml (6 molar excess) of triethylamine was added (the acetic anhydride and triethylamine were dry and distilled). The solution temperature was raised to 60°C for 24 hours before cooling and precipitating the polyimide in methanol followed by washing with diethyl ether. The resulting powder was dried under vacuum (~5 torr) at 200°C to remove residual water and solvent.

3.4.3 Solution Imidization of High Molecular Weight 4,4'-bis [4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPEDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

A general scheme for polyimides synthesized by the solution imidization route is shown in Scheme 3.4.3.1.



Scheme 3.4.2.1 Chemical Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)



Scheme 3.4.3.1 Solution Imidization of High Molecular Weight 4,4'-bis[4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPEDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

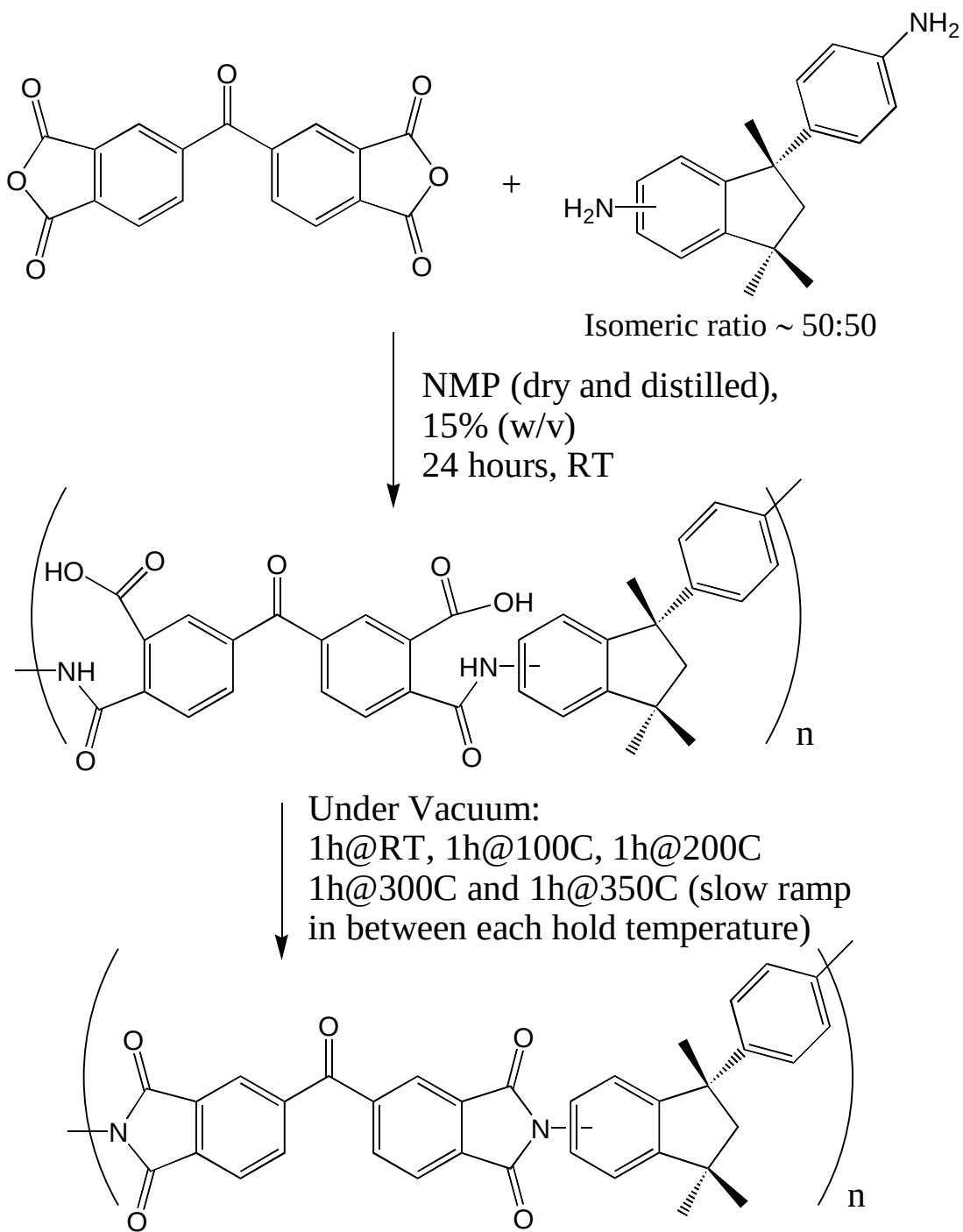
A typical example is as follows. To a flame dried three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap with a condenser (Figure 3.4.1.1), 2.0032g (18.5 mmol) of m-PDA was added and dissolved in 25 ml of dry and distilled NMP. To this homogeneous solution, 8.8620g (0.0185 moles) of BPEDA was slowly added along with 32ml of NMP (19wt% (w/v)). After being stirred for 24 hours at room temperature, the resulting polyamic acid was thermally imidized in solution. The azeotroping solvent, dry and distilled *o*-DCB, used to facilitate the removal of water produced during the reaction was used in the following ratio: NMP:*o*-DCB/5:1. The *o*-DCB was also used to fill the reverse Dean-Stark trap to maintain a constant solvent volume inside the flask. The polyamic acid solution was thermally imidized at 180°C for 24 hours before being cooled and poured into methanol to precipitate the polymer which was subsequently washed with diethyl ether.

3.4.4 Thermal Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

A general scheme for polyimides synthesized by the thermal imidization route is shown in Scheme 3.4.4.1.

A typical example is as follows. To a flame dried three-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap with a condenser (Figure 3.4.1.1), 0.9892g (3.7 mmol) of DAPI was added followed by 15ml of dried and distilled NMP. Once dissolved, 1.1965g (3.7 mmol) of BTDA was slowly added to the solution over a 30 minute period. The BTDA was rinsed in with 16.4ml of NMP to give a total weight percent of 15% (w/v). The solution was stirred for 24 hours at room temperature to form the polyamic acid of DAPI and BTDA.

The following thermal imidization schedule was performed on the polyamic acid cast from solution onto a glass plate: (under vacuum with slow ramping between each hold temperature) 1 hour at RT, 1h at 100°C, 1h at 200°C, 1h at 300°C and 1h at 350°C.



Scheme 3.4.4.1 Thermal Imidization of High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

The final imidization temperature depended on the T_g of the resulting polymer. As a general rule, the final imidization temperature must be $>20^\circ\text{C}$ above T_g . Following imidization, the polyimide film was removed from the glass plate with a small addition of water. The film was then redried at 200°C under vacuum for more than 12 hours.

3.5 Synthesis of Controlled Molecular Weight Polyimide Oligomers

Controlled molecular weight polyimide oligomers were synthesized by the ester-acid method. The stoichiometry of the monomers was varied according to the Carothers Equation to achieve the various desired molecular weight oligomers.

The Carothers Equation:

$$\langle X_n \rangle = N_o / [(1/2) * (2N_o - N_o p f_{av})] = 2 / (2 - p f_{av}) = 2 / (2 - f_{av}) \quad (\text{when } p = 1)$$

where,

$\langle X_n \rangle$ = the number average degree of polymerization,

p = the extent of reaction of the functional groups, and

$f_{av} = 4r/(r+1)$, $r = N_A/N_B$ for AA and BB type monomers with BB as the excess component or, $r = N_A/(N_B + N_B')$, when N_B' of monofunctional B endcapper is used.

Reorganization yields,

$$\langle X_n \rangle = (1 + r) / (1 - r).$$

A typical polymerization procedure for an amine terminated polyimide oligomer with a number average molecular weight of 5,000 g/mole is as follows: To a 250ml 3-necked round bottom flask, equipped with a mechanical stirrer, nitrogen inlet and a reverse Dean-Stark trap with a condenser (Figure 3.4.1.1), 14.8183 g (2.85 mmol) of BPADA was charged and rinsed in with 55ml of ethanol and 3ml of triethylamine. Under refluxing conditions, the ethyl ester-acid of the dianhydride was formed. After approximately one hour, the excess ethanol and triethylamine was distilled leaving a viscous ester-acid mixture. The diamine, *m*-PDA, was added to this mixture in the calculated stoichiometric offset amount, 3.4518 g (3.19 mmol), and washed in with NMP/*o*-DCB (5/1) to give twenty weight percent solids. The trap was drained and filled with the azeotroping solvent, *o*-DCB. The temperature was then raised to 180°C to obtain fully cyclized imide linkages.²¹ Within a few minutes, distillation of ethanol and water was observed as the amic acid was formed, followed quickly by imidization.

The solution was cooled after 24 hours. The polymer was precipitated in stirred methanol, then was filtered and washed with methanol and diethyl ether. The resulting powder was dried under vacuum (~5 torr) at 180°C for 24 hours.

CHAPTER 4 RESULTS AND DISCUSSION

This chapter is comprised of five major sections. The first section addresses monomer syntheses involved in this research, including diaminophenylindane, triaminophenylindane and dihydroxyphenylindane. The second section details the synthesis, molecular weight and thermal characterization of several novel polyimides which were targeted for their potential advantages as permselective membranes. Following the discussion of characterization, the O₂/N₂ permselective behavior of these materials is presented.

The third section of this chapter reports the synthesis and characterization of several novel polyimides containing hydroxyl moieties in the repeat unit of the polymer. This is followed by the fourth section, which discusses the thin film O₂/N₂ permselectivity of these systems. Finally, the last section covers applicable crosslinking mechanisms for semipermeable membranes.

4.1 Monomer Synthesis

4.1.1 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane and 5,6-diamino-(4-aminophenyl)-1,3,3-trimethylindane (DAPI and TAPI) Synthesis

The synthesis and basic characterization of DAPI was presented earlier in section 3.2.2. The overall yield for this reaction, starting with α -methylstyrene, was ~35%. The low yield was largely attributed to the initial step in the synthesis, the dimerization of α -methylstyrene, which gave a relatively low yield of 50%. The product, 1-phenyl-1,3,3-trimethylindane, was thought to be a racemic mixture of both the R and S configurations. By NMR the two configurations are chemically equivalent. Although it would be worth investigating, separation of these configurations was not pursued.

1-Phenyl 1,3,3-trimethylindane (phenylindane) appears to be especially susceptible to addition of a second nitro group thereby yielding the undesired trinitro

compound 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (TNPI) (which produced TAPI after reduction). The probability of nitrating twice on the same ring is unlikely if the nitrating species is charged in a 2:1 mole ratio (HNO_3 :phenylindane).

The synthetic procedure for DAPI and TAPI are very similar and differ only in percent solids content and in the ratio of chloroform to sulfuric acid. In each case, the amount of nitric acid was held constant (2:1, HNO_3 :phenylindane). The procedure to form TNPI yielded a mixture of the tri-, di- and mono- substituted products. TNPI was easily purified by recrystallization from ethanol. The synthesis of TNPI has not been reported in the literature.

Upon changing the chloroform:sulfuric acid ratio from 2:1 to 2:3, the resulting product became predominantly tri-substituted. Although details of this heterogeneous reaction need clarification, it is possible that by increasing the acid phase the likelihood of material diffusing to the chloroform/acid interface, where it can react, is also reduced.

4.1.2 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI) Synthesis

One of the objectives of this research was to prepare new monomers for tailoring the chemical structure of polyimides to impart a simultaneous increase in their oxygen permeabilities and oxygen/nitrogen selectivities. During the investigation of diaminophenylindane (DAPI), it was noticed that DAPI, in combination with the proper dianhydride, yielded films with both good permeability and good selectivity. From this starting point, effort was placed on synthesizing other related diamines which incorporated the phenylindane structure. It was thought that by incorporating the phenylindane structure into the polyimide backbone using a monomer with the modified structure of DAPI, the favorable characteristics of DAPI could be further developed. Polyimides based on these types of monomers would be expected to exhibit high T_g s, low solution and melt viscosities, and high thermal stability due to the presence of the phenylindane structure. The resulting polymers would also be expected to show good gas selectivity and, perhaps, high permeabilities due to the rigid and extremely bulky nature of phenylindane.

Synthesis of phenylindane containing monomers and/or their polymerization has been reported by a number of authors (Figure 4.1.2.1).²⁷¹⁻²⁸⁶ Polyimides have been synthesized from diaminophenylindane^{285,286} or diamines resulting from the reaction of dihydroxyphenylindane²⁷¹⁻²⁸⁸ (DHPI) with either o/p-chloronitrobenzene or dinitrobenzene.²⁸¹⁻²⁸⁴ Dianhydrides from dihydroxyphenylindane (DHPI) and 4-fluorophthalic anhydride have also been reported.²⁷⁴ Although polyimides utilizing DHPI based monomers have been reported in the patent literature, there is either very little or no mention of fundamental polyimide characterization, such as molecular weight or glass transition temperature. Therefore, DHPI based monomers were of interest in this thesis research.

Successful synthesis of DHPI disclosed in this thesis has opened several routes to obtaining monomers for potentially improving gas permselectivity of polyimides. Three likely monomeric candidates, all originating from DHPI, are shown in Scheme 4.1.2.2. Of the three potential candidates, the bis(o-aminohydroxy)-Containing monomer (1) has not been previously reported. Monomers (2) and (3) have been reported, but very few of their characteristics have been disclosed.

The details of the synthetic procedure used to prepare DHPI as well as basic structural characterization may be found in the experimental section. The base catalyzed cracking of bisphenol A was carried out at elevated temperatures, followed by dimerization of the resulting isopropenyl phenol, which was facilitated by an acid catalyst. This procedure gave an overall yield of ~30%. Obvious factors influencing the yield were the choice of base and acid catalysts, which may control the rate of oligomer formation. The base and acid catalysts selected were based on literature procedures. However, optimization of these reagents may improve the observed yield.

The desirable properties of polyimides containing the trimethylphenylindane structure indicate that future work should encompass synthesis and investigations of the three monomers derived from DHPI. This thesis work, however, did not develop routes to form the polyimide precursors shown in Scheme 4.1.2.2.

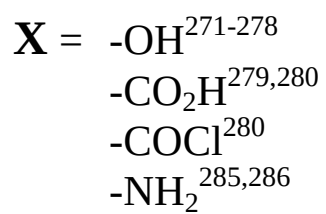
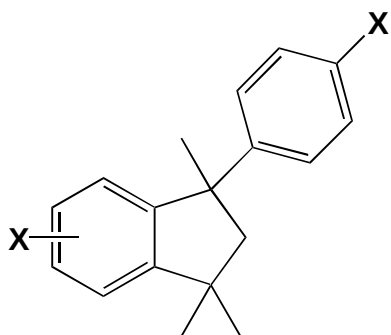
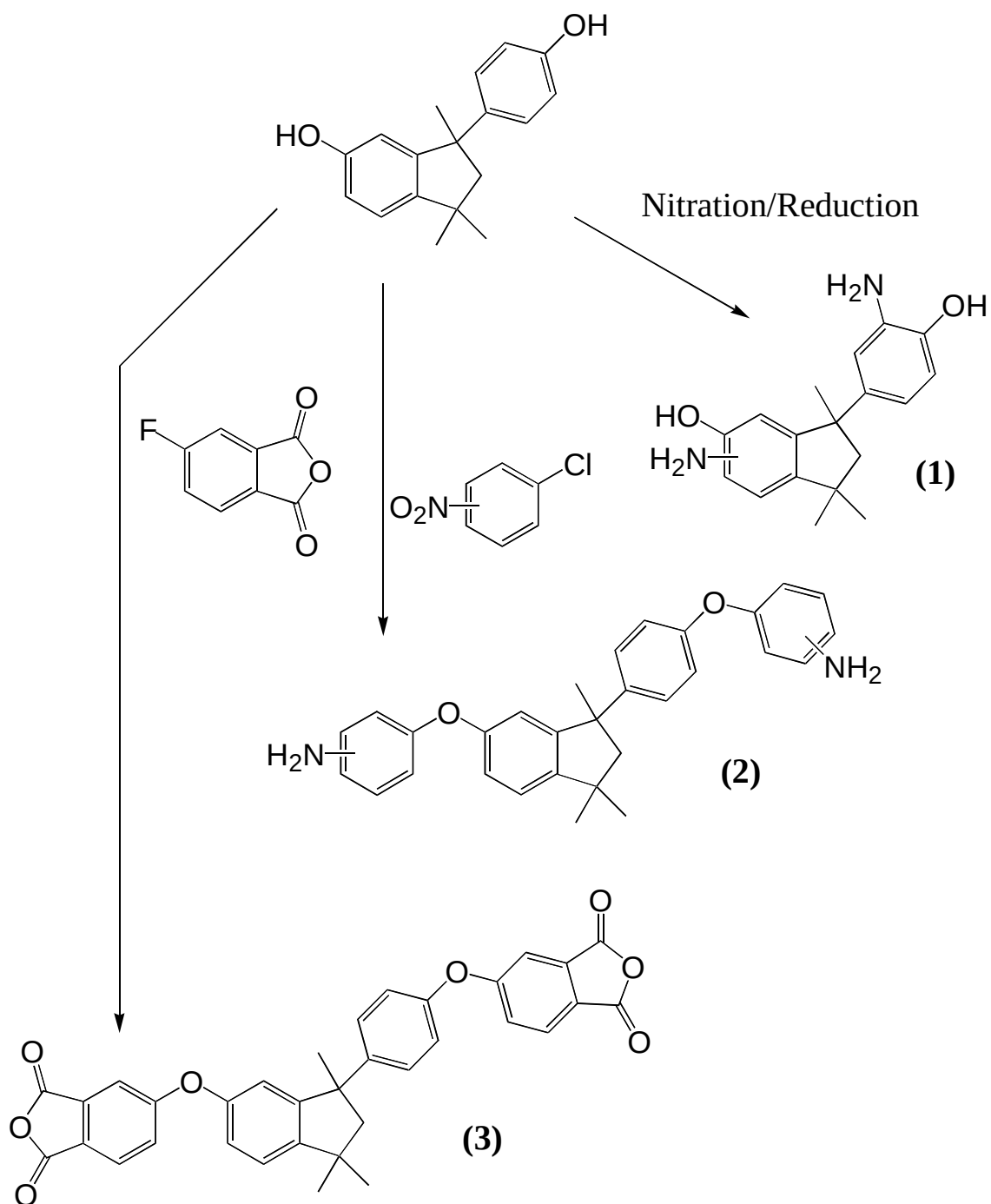


Figure 4.1.2.1 Reported Monomeric Derivatives of 1-phenyl-1,3,3-trimethylindane



Scheme 4.1.2.1 Proposed Polyimide Monomers from Reactions with 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI)

4.2 Molecular Weight and Thermal Characterization of Novel Polyimides

Polyimides containing novel diamines and/or dianhydrides were investigated for their potential use as semipermeable membranes for gas permselectivity. Monomer selection for these materials was based upon previous observations reported in the literature. Through extensive experimentation, the two following criteria have emerged to guide synthetic researchers in their efforts to improve permselective membranes (Section 2.5).²³³⁻²³⁶ This information set the stage for monomer selection. Monomers were selected to yield highly rigid polymer backbones, while simultaneously increasing interchain spacing with bulky groups. This section details the molecular weight and thermal characteristics of a number of polyimides satisfying these requirements. Following these characteristics, the permselective behavior of the polymer thin films will be presented.

4.2.1 Characterization of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides via Ester-acid Solution Imidization³⁰¹

Polyimides are well known for their excellent thermal and oxidative stability as well as excellent mechanical properties.²⁸⁷⁻²⁹⁰ Due to their wide utility as matrix resins, coatings and adhesives for aerospace and microelectronic applications, a broad range of synthetic routes have been developed in an attempt to facilitate easier and more cost efficient syntheses.

The two most commonly used routes suitable for amorphous polyimide preparation are chemical and solution imidization. Both require the drying of commercially available solvents, since their water content can potentially upset the monomeric anhydride/amine stoichiometry and lead to unpredictable molecular weights.

Our research group has been interested in developing improved polyimide material systems for some time.^{130,291,292} In an effort to alleviate dianhydride water sensitivity, and subsequent hydrolysis, a method has been developed based on earlier

work²⁸⁷⁻²⁹⁰ which involves the pre-reaction of anhydride moieties with ethanol in the presence of a tertiary amine catalyst.^{291,292} The ester-acids formed can be prepared in the presence of commercially available solvents and are very tolerant of water content in both the solvents and reactor. In addition, the ester-acids are more soluble in organic solvents than their dianhydride parents. The factors necessary for the formation of high molecular weight amorphous polyimides via this route were recently reviewed.^{130,291,292} It was shown that ester-acids are conveniently prepared from the monomeric dianhydrides in the presence of ethanol. At an elevated temperature, the dianhydride was reformed, followed by attack of an aryl diamine and, finally, cyclodehydration ensues to form imide.

One objective of this research was to broaden the applicability of the ester-acid solution imidization route to encompass a system which has been reportedly prepared via chemical imidization, namely, CIBA's XU218.^{285,293} The latter is prepared from benzophenone tetracarboxylic dianhydride (BTDA) and a mixture of the C-5 and C-6 isomers of diaminophenylindane (DAPI), shown in Figure 4.2.1.1. For our purposes, NMR and HPLC (Figure 4.2.1.2) validated monomer grade DAPI. Both of these techniques show the DAPI to be present in a near 50:50 mixture of the C-5 and C-6 isomers, which is in good agreement with previous findings.^{285,286}

Polyimides containing DAPI were one of the first truly soluble, fully cyclized systems. DAPI is of particular interest due to its inherent asymmetry and non-planarity which produces highly soluble polyimides with even the most rigid dianhydrides. At the same time, the polymers are quite rigid which is evident from the high glass transition temperatures observed for these systems. The absence of aliphatic, oxidatively susceptible benzylic hydrogens and adjacent aliphatic carbons bearing hydrogens may impede facile degradation and allow these systems to show good thermooxidative stability.

The dianhydride monomers utilized in the synthesis of DAPI containing polyimides were all commercially available and are shown in Figure 4.2.1.3. The synthesis of DAPI, which is the acid catalyzed dimerization of α -methylstyrene, and subsequent nitration and reduction, is described in the experimental section of this report.

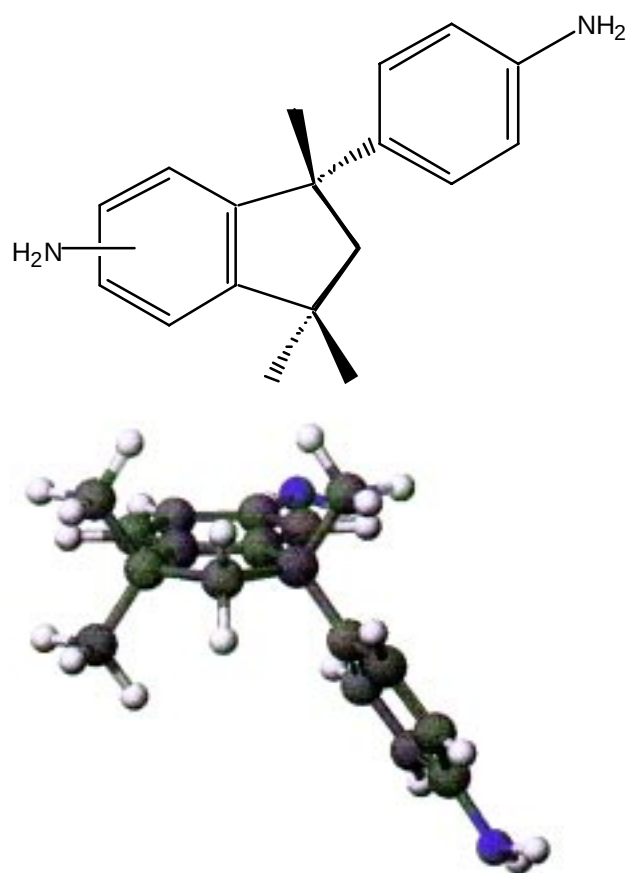


Figure 4.2.1.1 A 3-D Model of Diaminophenylindane

Isomeric Ratio via HPLC: 50% (6): 50% (5)

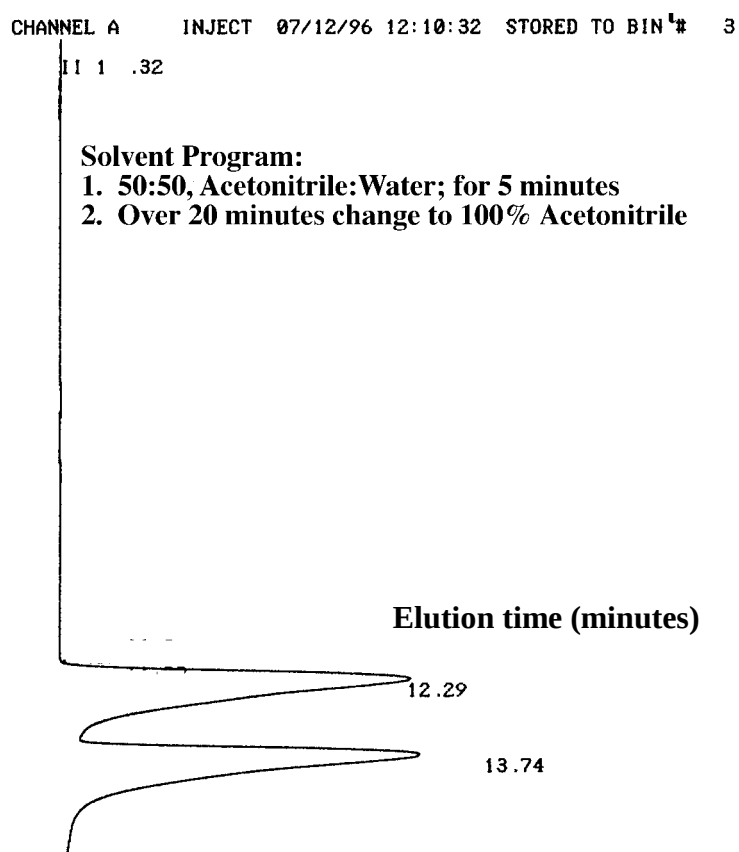
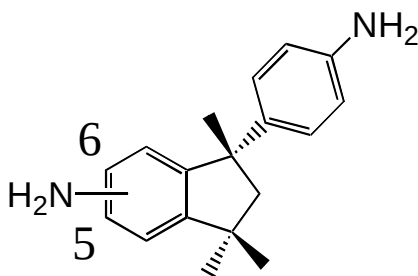


Figure 4.2.1.2 High Performance Liquid Chromatography of DAPI

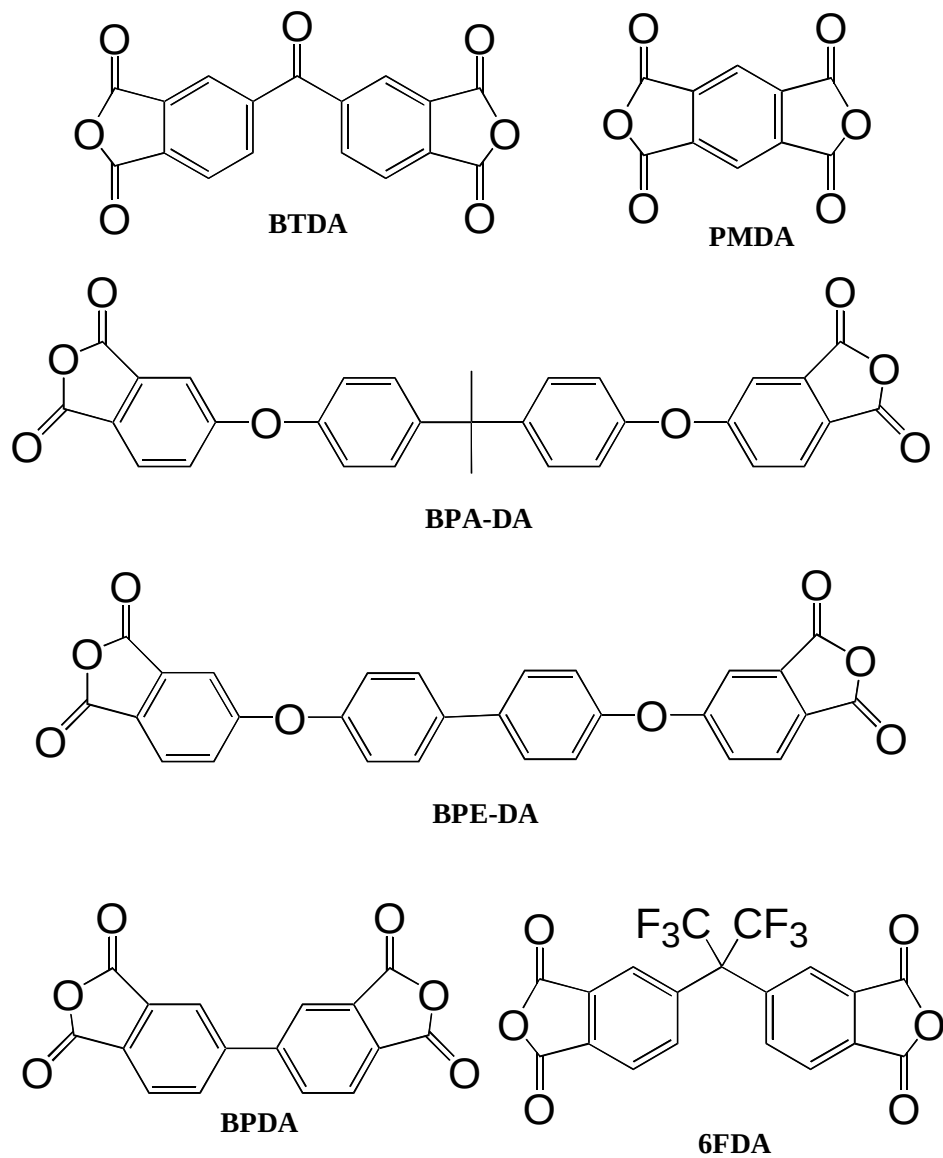


Figure 4.2.1.3 Monomers Used with DAPI for the Synthesis of Polyimides

The polyimides were prepared by forming the ester-acid precursor, followed by the addition of diamine and then solution imidization. The resulting polymers were also cast from an NMP solution to form tough creasable films. The conversion of the poly(amic acid)s to the fully cyclized polyimides was monitored by FTIR.²⁹⁴⁻²⁹⁶ Cyclodehydration was confirmed by the appearance of absorption modes at approximately 1785, 1727, 1370, and 733 cm^{-1} due to symmetric C=O, asymmetric C=O and C-N stretching, and ring deformation, respectively (Figure 4.2.1.4). These wavelengths corresponded to previously reported imide ring adsorptions.²⁹⁷⁻³⁰⁰ Complete cyclization was also evident by the lack of amide C=O (1640 cm^{-1}) and N-H (1550 cm^{-1}) peaks.^{155,160} A representative NMR of DAPI based polyimides is given in Figure 4.2.1.5.

For each of the polymers, high molecular weights have been achieved as was confirmed by GPC (Table 4.2.1.1). Earlier reports in the literature of high molecular weights were in reference to polystyrene standards and not universal calibration. A typical raw chromatogram for DAPI/6FDA is shown in Figure 4.2.1.6. It shows a unimodal molecular weight distribution with a polydispersity index of about two, which is expected for step-growth polymerizations.

The polymer powders were thermally analyzed by DSC and TGA and the results are summarized in Table 4.2.1.1. DSC revealed the materials to have high and broad T_g values occurring over a 30°C range (Figure 4.2.1.7). The breadth of this transition is most likely due to an isomeric effect, as DAPI has four isomers. The more rigid anhydrides, such as PMDA and BPDA, would be expected to show the highest T_g s, as indeed they do. The more flexible dianhydrides show lower glass transition temperatures. The T_g s increase in the following order: BPADA < BTDA ~ 6FDA < PMDA < BPDA.

Preliminary assessment of the thermal stability of these polymers was also determined by TGA in the presence of air. The primary factors which contribute to heat resistance are primary and secondary interactions, resonance stabilization, molecular symmetry and the mechanisms of bond cleavage. As a class, polyimides show excellent

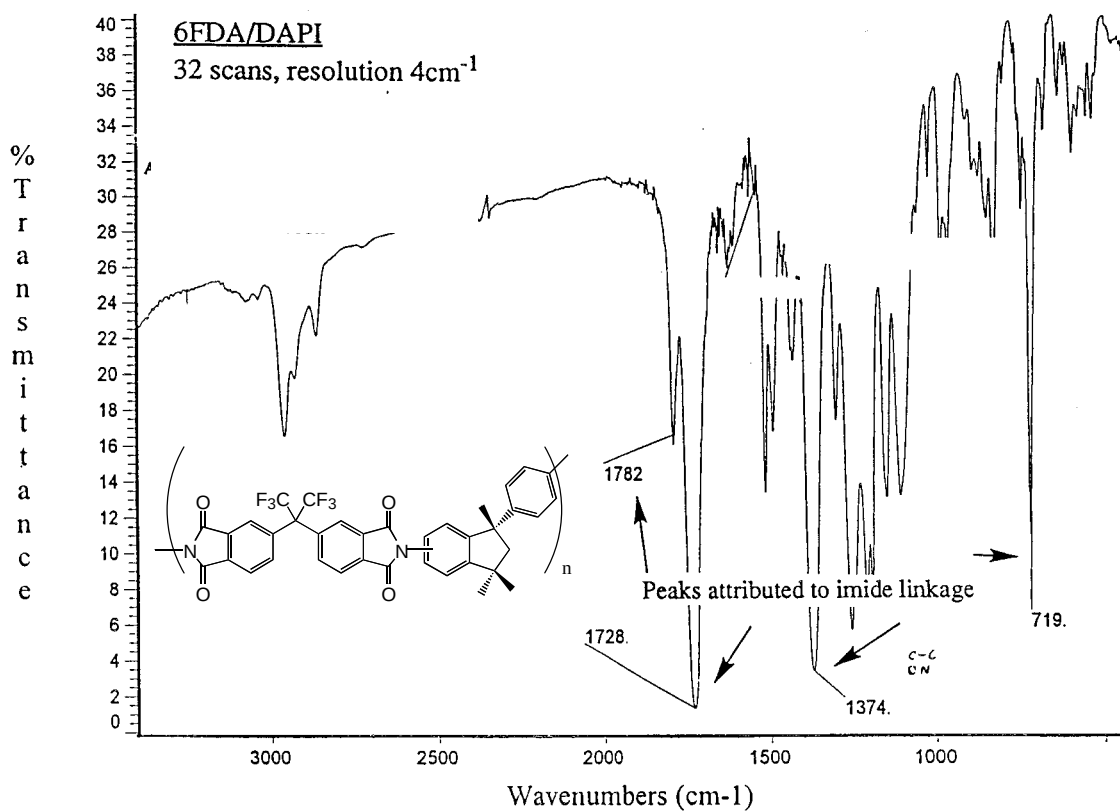


Figure 4.2.1.4 FTIR Spectrum of High Molecular Weight 6FDA/DAPI Showing Absorptions Due to Cyclic Imide Functionalities

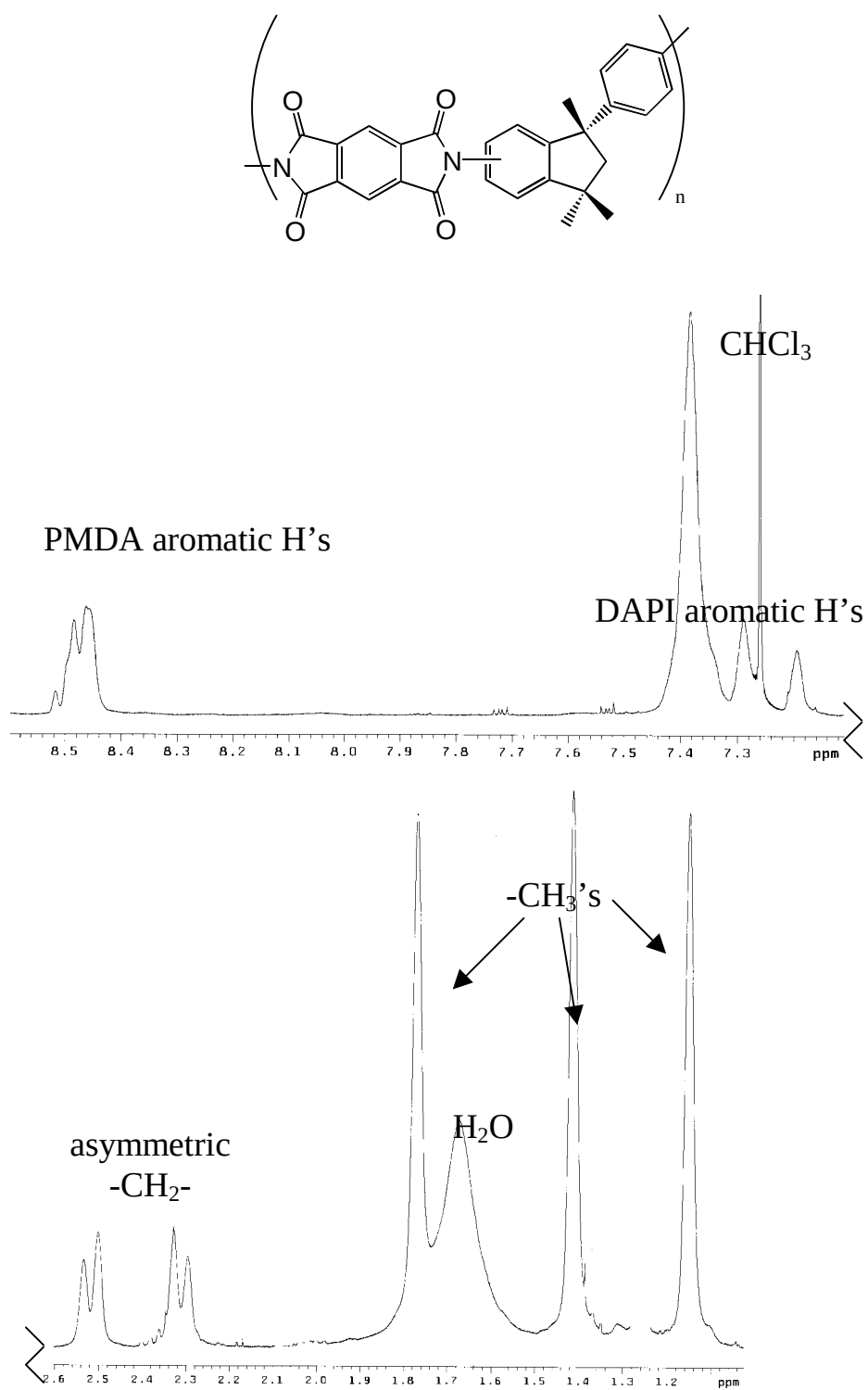
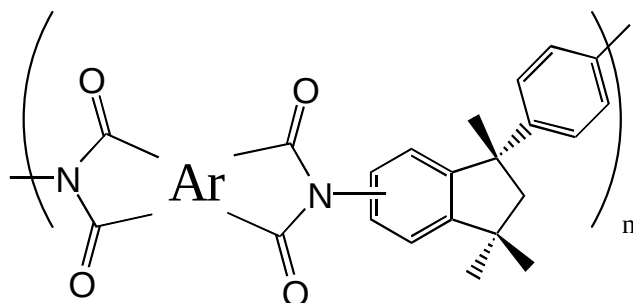


Figure 4.2.1.5 High Resolution ^1H NMR of DAPI/PMDA

Table 4.2.1.1 Molecular Weight and Thermal Analysis of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides



Dianhydride	Molar Ratio	M _n (K) ⁺ (avg.)	M.W.D.	T _g (°C)*	TGA 5% Wt. Loss (°C)**
BPADA	1:1	29.9	1.7	247	536
BPEDA	1:1	27.5	2.4	288	---
BTDA	1:1	32.5	1.9	333	525
6FDA	1:1	35.1	1.9	331	493
BPDA	1:1	28.5	1.8	368	558
PMDA	1:1	26.1	1.7	354	540

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 20°C/min

** heating rate of 10°C/min in air

Gel Permeation Chromatography
 Waters 150-C ALC/GPC
 Refractive Index Detector
 Viscotek Model 100 Viscosity Detector
 Solvent: NMP + 0.05M P₂O₅

DV Chromatogram

JB2206 DP

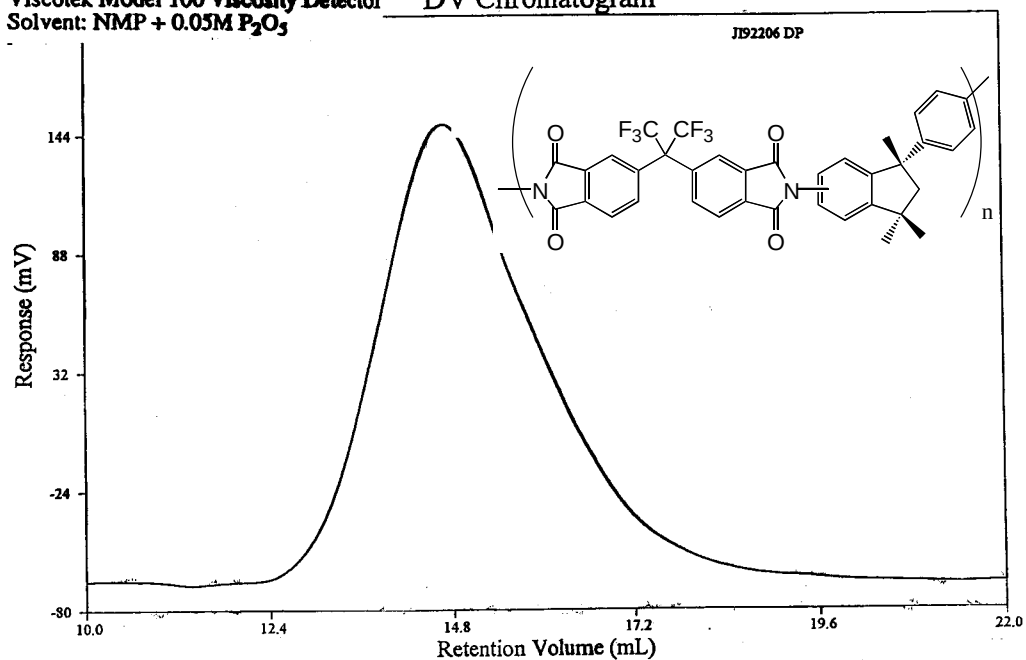
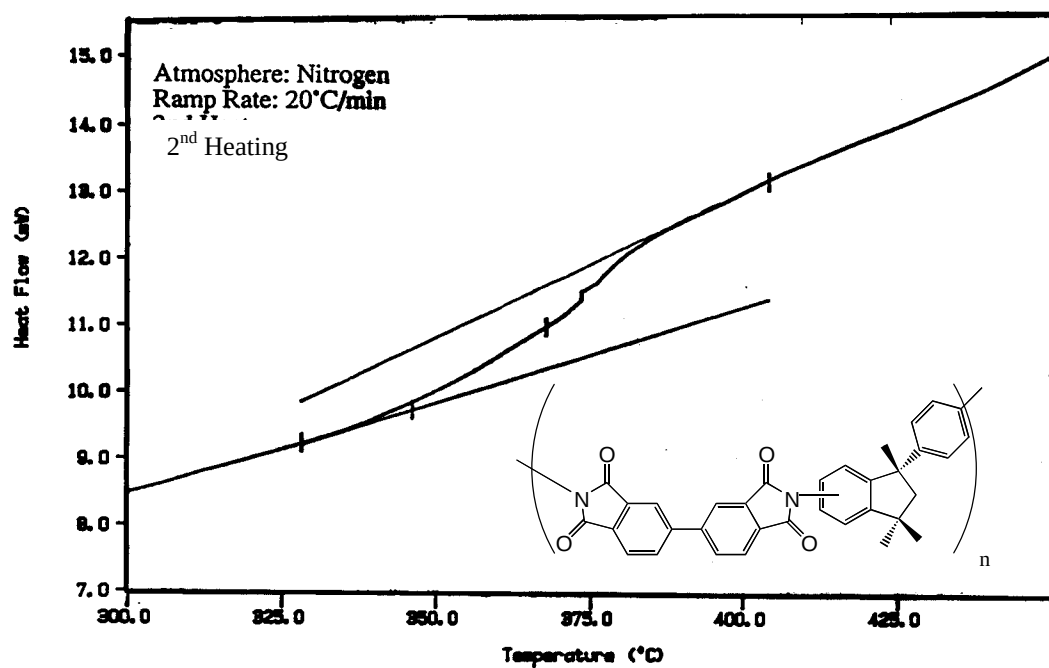


Figure 4.2.1.6 Raw GPC Chromatogram of High Molecular Weight 6FDA/DAPI Polyimide



resistance to thermal degradation, and for these polyimides, the 5% weight loss occurred around 500°C (Figure 4.2.1.8 and Table 4.2.1.1).

The microelectronic industry screens thermally stable polymers by isothermal weight loss of the polymer at 400°C, under nitrogen, over a two hour time interval. Surprisingly, the minimal weight loss shown by the high molecular weight 6FDA-DAPI system under these conditions was comparable to that of Kapton (PMDA/ODA) (Figure 4.2.1.9). This preliminary test suggested that this material may be able to withstand the harsh thermal environment required for certain electronic applications, despite the partially aliphatic nature of the polymer backbone. Unlike Kapton, 6FDA-DAPI has the advantage of being soluble.

Polymer solubility is presented in Table 4.2.1.2. Nearly all of these polymers were soluble in NMP, DMAc, CHCl₃, CH₂Cl₂ and THF, at relatively high solids content (10 wt%). Only in the more rigid systems, PMDA/DAPI and BPDA/DAPI, was dissolution not observed in THF. The good solubility in a number of solvents is attributed to the isomeric, asymmetric and non-planar structure of DAPI.

Refractive index values for the high molecular weight DAPI based polyimides are shown in Table 4.2.1.3. A polymer containing a greater percentage of polarizable groups, such as oxygen, nitrogen and aromatic rings, will display a higher refractive index value. Polymers with less polarizable functionalities, such as fluorine and aliphatic carbons, will have a lower refractive index. As expected, the lowest refractive index is observed for 6FDA/DAPI due to the six fluorine atoms per repeat unit and the aliphatic groups in DAPI. The polyimides based on DAPI were found to have increasing refractive indices in the following order: 6FDA<PMDA~BPADA<BTDA<BPDA.

To a first approximation, the dielectric constant for these presumably isotropic polymers can be estimated by the square of the refractive index³⁰⁴. The lowest dielectric constant value was found for the 6FDA/DAPI system, which had a value of 2.47. In microelectronics a low dielectric constant is desired to prevent “cross-talk” between conducting vias. A polyimide with a dielectric constant this low may be attractive for this industry.

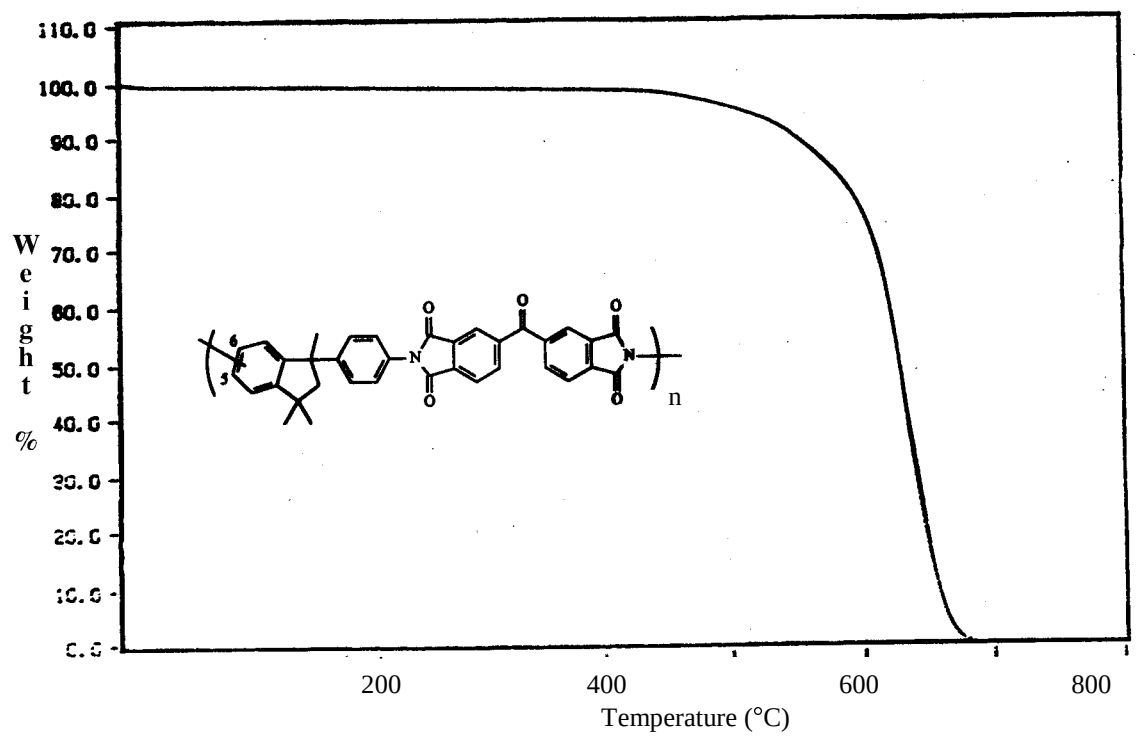


Figure 4.2.1.8 Dynamic TGA of High Molecular Weight BTDA/DAPI in Air (10°C/min)

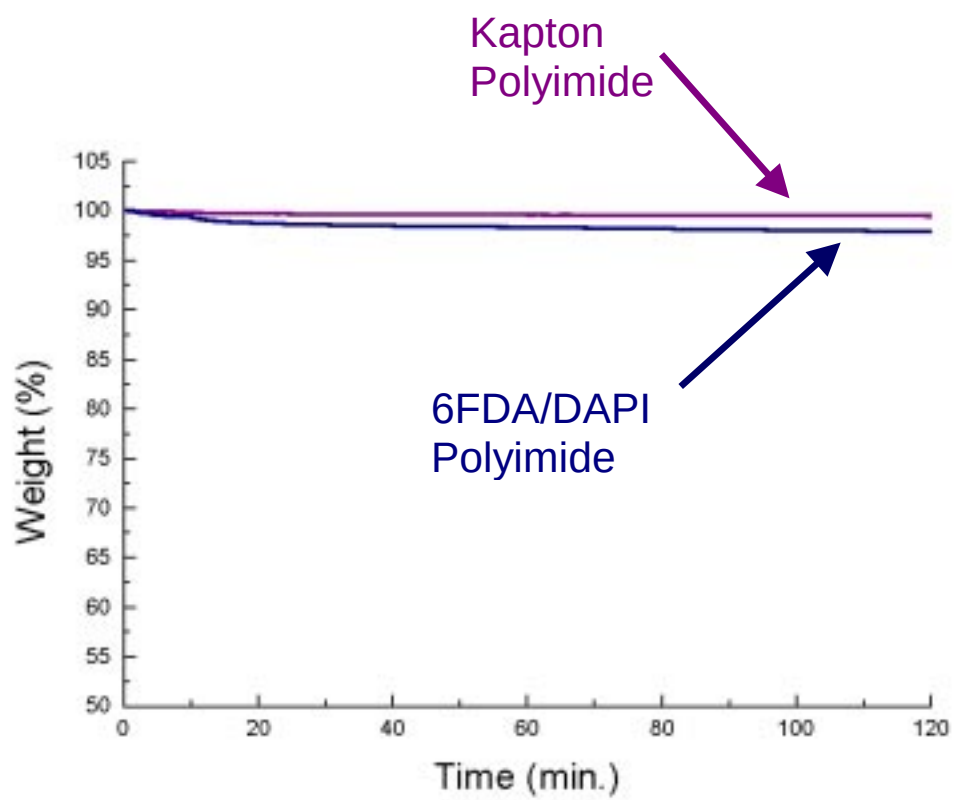
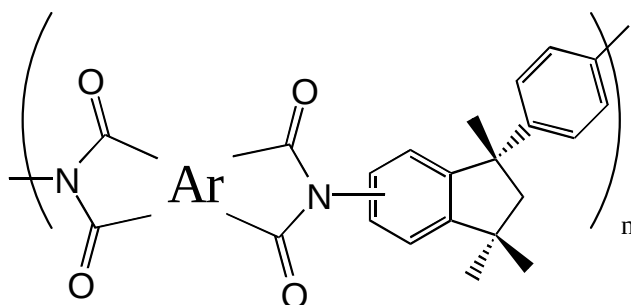


Figure 4.2.1.9 Isothermal TGA of PMDA/ODA Based Kapton and 6FDA/DAPI Based Polyimide at 400°C Under Nitrogen

Table 4.2.1.2 Solubility of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)
Based Polyimides in Common Solvents

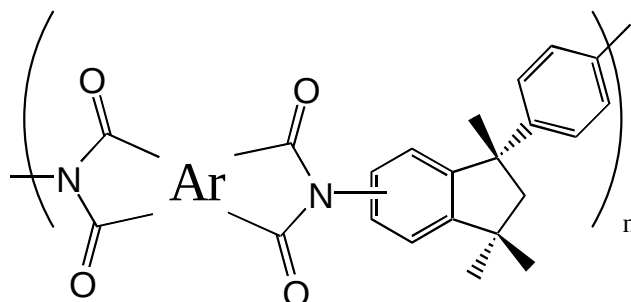


Dianhydride	NMP	DMAc	CHCl ₃	CH ₂ Cl ₂	THF
ULTEM(control)	S	S	S	S	I
BPADA	S	S	SS	S	S
BTDA	S	S	S	S	S
6FDA	S	S	S	S	S
BPDA	S	SH	S	S	SW
PMDA	S	SH	S	S	SW

S - soluble at RT; SS-slightly soluble at RT;
SW - swelled; SH - soluble in hot solvent; I -
insoluble

Solubility test done at 10% solids

Table 4.2.1.3 Refractive Index Values and Dielectric Constant Approximation of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides



Dianhydride	Refractive Index (n)	Dielectric Constant Approx. (n ²)
6FDA	1.571	2.47
PMDA	1.623	2.63
BPADA	1.629	2.65
BTDA	1.639	2.69
BPDA	1.657	2.75

Standard Deviation for RI measurement, ± 0.001

4.2.2 Effect of Imidization Method on High Molecular Weight 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

High molecular polyimides consisting of DAPI and BTDA were synthesized using three different routes. Polyimides obtained via the ester-acid and chemical imidization methods were soluble while the thermally imidized system was insoluble in hot NMP. Insolubility may have resulted from a small amount of side reactions such as crosslinking³⁰³. The resulting molecular weights and thermal properties of the polyimides are presented in Table 4.2.2.1. The soluble polyimides, prepared via the ester-acid and chemically imidization methods, were found to have high molecular weight by GPC.

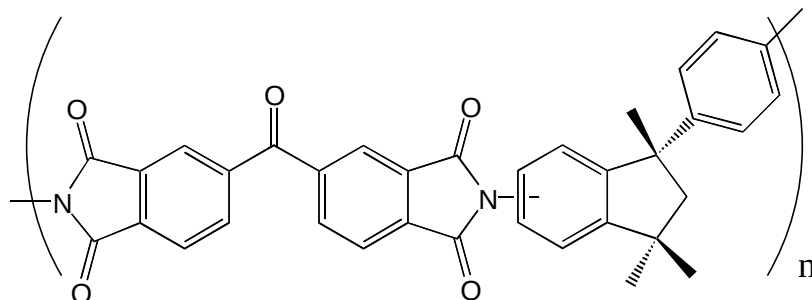
A noticeable difference in thermal behavior was observed for the chemically imidized polyimide with respect to the T_g and 5% weight loss values. Although there was no noticeable difference in the FTIR spectra of the polymers synthesized by the different methods, it is possible that the lower T_g and lower 5% weight loss values resulted from residual amide acid groups present in low concentration and, therefore, below the detection limit of the infrared instrument (i.e. <1%).

The polyimides synthesized using the ester-acid and thermal imidization routes have similar T_g and 5% weight loss values. It is possible that the slight differences observed may have resulted from small structural changes in the thermally imidized sample, since it is known that carbonyl functionalities may abstract labile protons such as those present in the DAPI when exposed to UV light or high temperatures^{1,303}.

4.2.3 Effect of the DAPI Isomeric Ratio on Thermal Properties

It was of interest to investigate the effect of altering the 5- and 6-amino isomeric ratio of DAPI from the normal equimolar mixture. To increase the ratio of one of the isomers relative to the other, the diamine was recrystallized multiple times from toluene.²⁸⁶ Three different isomeric mixtures were studied in polycondensations with

Table 4.2.2.1 Molecular Weight and Thermal Characterization of 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA)/5(6)-Amino-(4'-aminophenyl)-1,3,3-trimethylphenylindane (DAPI) Based Polyimides



Imidization Method	Molar Ratio	M _n (K) ⁺ (avg.)	M.W.D.	T _g (C°)*	TGA 5% Wt. Loss (C°)**
Chemically	1:1	21.1	1.9	311	457
Thermally	1:1	insoluble	---	324	510
Ester-Acid	1:1	32.5	1.9	333	525

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 20°C/min

** heating rate of 10°C/min in air

BTDA. The following are the ratios used with regard to 6-amino:5-amino DAPI isomers: 60:40, 50:50 and 30:70 (ratios determined by HPLC). In order to obtain completely soluble polyimides required for gas membrane production, it was found that the isomeric ratio could not be below 30:70 (6:5) due to reduced solubility observed with regard to the BTDA/DAPI polyimide.

Polycondensation and chemical imidization of the DAPI/BTDA systems produced polyimides with high molecular weight as shown in Table 4.2.3.1. There were no noticeable differences in either the thermal behavior or molecular weight values for the series. Hence, the results suggested that a slight change in the isomeric ratio had negligible effect in altering the polymer properties such as T_g , 5% weight loss in air, M_n and molecular weight distribution.

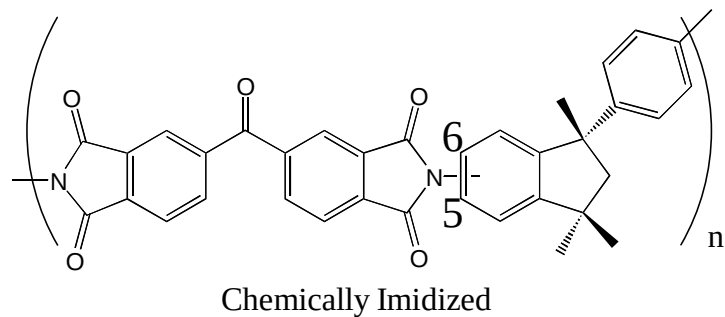
4.2.4 Biphenylether Dianhydride (BPEDA) and Bisphenol A Dianhydride

(BPADA) Based Polyimides

Anhydride functional groups in BPADA are connected through an isopropylidene bridge, whereas the anhydride functional groups in BPEDA are linked via a biphenyl unit. The two flexible ether linkages in BPADA and BPEDA afforded sufficient backbone mobility to yield soluble polyimide systems. Monomer composition, thermal characteristics and molecular weight values are reported in Table 4.2.4.1. The BPEDA based polymers were synthesized via the high temperature solution imidization method, while the BPADA based polyimides were synthesized by the ester-acid solution imidization method. Each of the polyimides was high molecular weight and had polydispersities near two.

Earlier, the polyimide derived from BPADA/DAPI was shown to have a T_g of 288°C. Substitution of *m*-PDA for DAPI reduced the T_g from 288°C to 254°C. Even though *m*-PDA is also very rigid (i.e., like DAPI), the observed decrease in T_g resulted from the smaller diamine, *m*-PDA, contributing a smaller weight percent to the polyimide repeat unit, and thus a smaller portion of its own character to the polymer chain. For the

Table 4.2.3.1 Molecular Weight and Thermal Characterization of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylphenylindane (DAPI) Based Polyimides Upon Altering the DAPI Isomeric Ratio



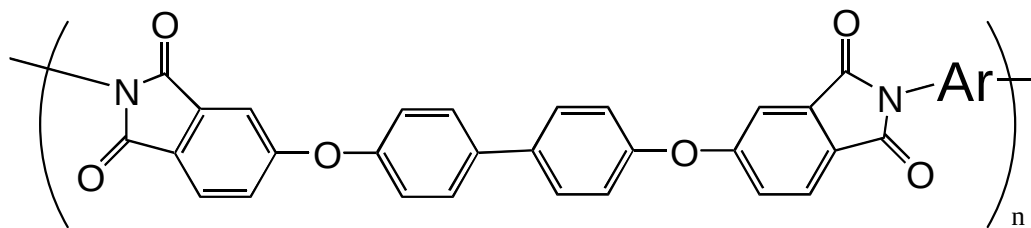
Isomeric Ratio (6:5)	Molar Ratio	M _n (K) ⁺ (avg.)	M.W.D.	T _g (°C)*	TGA 5% Wt. Loss (°C)**
60:40	1:1	26.3	2.2	311	456
50:50	1:1	21.1	1.9	311	457
30:70	1:1	26.5	2.0	312	449

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

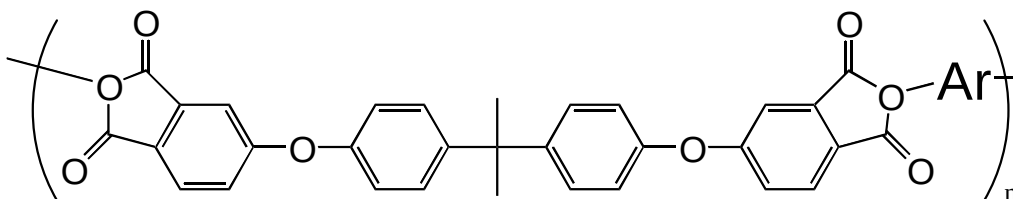
* 2nd heating; heating rate of 20°C/min

** heating rate of 10°C/min in air

Table 4.2.4.1 Molecular Weight and Thermal Characterization of High Molecular Weight 4,4'-bis [4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPE-DA) and 2,2'-bis [4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride (BPA-DA) Based Polyimides



-Ar-	Target M_n	M_n (K) ⁺ (avg.)	M.W.D.	T_g (C) [*]
DAPI	1:1	27.5	2.4	288 ^{**}
<i>m</i> -PDA	1:1	27.1	1.9	254
BPEDA:BPADA(1:1)/ <i>m</i> -PDA	1:1	18.5	2.1	234



-Ar-	Target M_n	M_n (K) ⁺ (avg.)	M.W.D.	T_g (C) [*]
DAPI	1:1	29.9	1.7	247 ^{**}
<i>m</i> -PDA	20K (offset)	17.2	1.9	215

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 10°C/min

** 2nd heating; heating rate of 20°C/min

BPEDA based polyimides, a difference of 32°C was observed by changing the diamine from DAPI to *m*-PDA.

Substituting BPEDA for BPADA in the BPADA/*m*-PDA polyimide, the glass transition temperature increases by 19°C due to the less flexible biphenyl link. The copolymer of BPEDA:BPADA (1:1) with *m*-PDA has a T_g approximately equidistant from the T_g reported for each of the homopolymers, 254°C (BPEDA/*m*-PDA) and 215°C (BPADA/*m*-PDA).

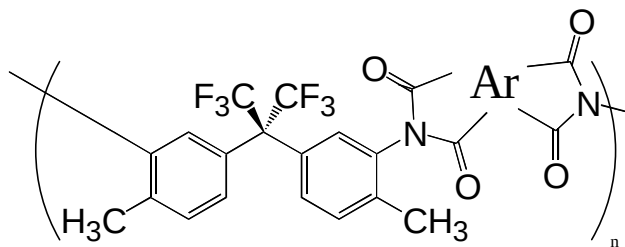
4.2.5 Polyimides Based on 2,2-Bis(3-amino-4-methylphenyl)hexafluoropropane (Bis-AT-AF)

Polyimides based on Bis-AT-AF were synthesized via high temperature solution imidization methods using NMP. The bulkiness and nonpolar nature of the hexafluoropropane moiety was expected to increase gas permeability, decrease the dielectric constant and yield soluble polyimides when combined with a variety of dianhydrides. The methyl substituent is also a potential site for crosslinking through UV initiated mechanisms.

Three dianhydrides were chosen in combination with Bis-AT-AF to yield soluble polyimides. These were: BPADA, BTDA and 6FDA. Table 4.2.5.1 details the molecular weight characterization and the thermal analysis of these materials. Analysis by GPC revealed high molecular weights for each of the polymers. Solution cast films from NMP were tough and creaseable.

The glass transition temperature for each of the polymers was found to be above 220°C (Table 4.2.5.1). The most flexible dianhydride, BPADA, had the lowest glass transition in the series due to the two ether links and the isopropylidene bridge. The more rigid dianhydride, 6FDA, had the highest T_g . Polyimides formed from Bis-AT-AF have T_g s in the following order: BPADA < BTDA < 6FDA. Decrease in polyimide thermal stability occurred due to the presence of more labile functionalities in the polyimide backbone (i.e., benzylic hydrogens). The pendant methyl groups present in the Bis-AT-

Table 4.2.5.1 Molecular Weight and Thermal Analysis of 2,2-bis(3-amino-4-methylphenyl)hexafluoropropane (Bis-AT-AF) Based Polyimides



-Ar-	Target M_n	M_n (K)⁺ (avg.)	M.W.D.	T_g (°C)[*]	TGA (°C)^{**}
BPADA	1:1	26.4	2.1	224	456
BTDA	1:1	28.2	3.0	239	462
6FDA	1:1	27.7	2.2	270	457

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 10°C/min

** in air, 10°C/min

AF polyimides reduced the 5% weight loss values typical of most polyimides (>500°C) to around 460°C.

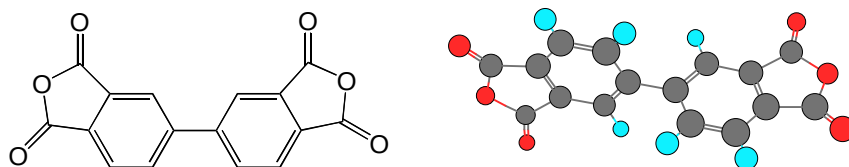
4.2.6 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione (6FDA) Based Polyimides

Polyimides containing 6FDA were of interest due to their excellent properties such as good solubility, low dielectric constant, low moisture sorption, good optical clarity and high gas permeability. Three dimensional models of 6FDA and biphenyl dianhydride (BPDA) molecules are shown in Figure 4.2.6.1. Clearly, the 6FDA structure appears to be much more bulky and bent when compared to BPDA. This structural difference often imparts solubility of 6FDA systems over BPDA polyimide analogs. Three diamines were chosen in combination with 6FDA to yield soluble, high T_g systems.

In Table 4.2.6.1, the molecular weight characteristics and thermal behavior are shown for these materials. The high temperature solution imidization route was used to form high molecular weight polymers from an equimolar ratio of diamine and dianhydride. Molecular weight distributions of 2.0 are shown in each case. In combination with *m*-phenylenediamine (*m*-PDA), 6FDA produced a polyimide having a T_g of 295°C. By increasing the chain rigidity with a bulky, highly rigid diamine, 9,9-bis(4-aminophenyl) fluorene (FDA), the T_g increased quite dramatically from 295°C to 369°C. Although *m*-PDA and FDA have comparable rigidities, the higher molecular weight diamine, FDA, contributed a greater amount of its “rigid” character to the polymer repeat unit as opposed to the smaller *m*-PDA. Thus, observation of higher T_g is the usual effect, which results from incorporating a higher molecular weight diamine was the observed increase in T_g . Another factor, which may also play a role in producing the high T_g of FDA/6FDA, is the inherent bulkiness of fluorene. The bulky substituent may hinder interchain molecular rotation and thereby increase the T_g .

The diamine, DDBT, is rigid and also possesses some bulky characteristics from the methyl groups and the two oxygens which protrude out of plane. The T_g of DDBT/6FDA was not obtainable due to initiation of polymer degradation in the DSC.

BPDA



6FDA

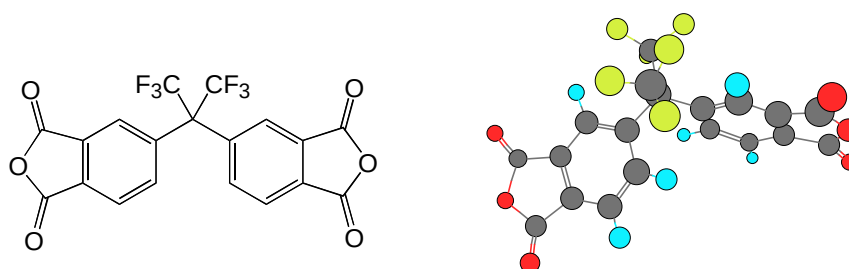


Figure 4.2.6.1 Three Dimensional Projections of 6FDA and BPDA

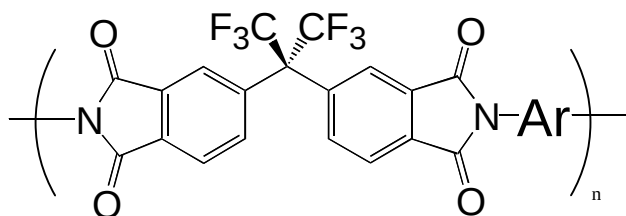


Table 4.2.6.1 Molecular Weight and Thermal Analysis of 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethyldiene]bis-1,3-isobenzene-furandione (6FDA) Based Polyimides

-Ar-	Target M _n	M _n (K) ⁺ (avg.)	M.W.D.	T _g (°C)*	TGA (°C)**
m-PDA	1:1	50	2.0	295	520
DDBT	1:1	31.7	2.0	>350	472
FDA	1:1	28.2	1.9	369	522

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 10°C/min

** in air, 10°C/min

The TGA results, as expected, showed good thermal stability for *m*-PDA/6FDA and FDA/6FDA, and a correspondingly reduced stability for DDBT/6FDA, which was partly attributable to abstractable benzylic protons.

4.2.7 Polyimides Derived from 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)

Homopolyimides containing DDBT were expected to yield high T_g s due to the inherent monomer rigidity. It was unclear if these polyimides would be soluble. Two dianhydrides, which are known to produce soluble polyimides in many cases, were chosen in combination with DDBT. The two systems, BPADA/DDBT and 6FDA/DDBT, were synthesized using high temperature solution imidization methods. Both polymers were soluble in the reaction solvent, NMP.

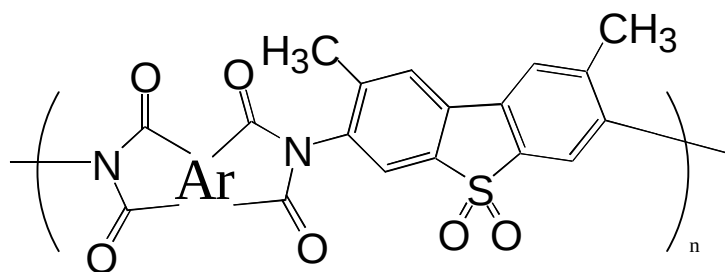
Molecular weight and thermal characterization is presented in Table 4.2.7.1. Even though the molecular weight for the BPADA/DDBT system was not high, i.e., <20,000g/mol, the polyimide could be solution cast from NMP to form creasable and ductile films. The glass transition temperature of BPADA/DDBT was found to be 313°C, which was about 95°C higher than that of the BPADA/*m*-PDA system. The rationale behind such a dramatic increase must be related to the extended rigid and planar nature of DDBT.

Each of these polymers had a 5% weight loss in air below 500°C resulting from, at least in part, the abstractable benzylic protons present in DDBT.

4.3 Gas Permselectivity Studies Performed on Novel Polyimides

Gas permeability through a semipermeable membrane is a product of the diffusion coefficient (a mobility factor) and solubility constant, which is the specific interaction of

Table 4.2.7.1 Molecular Weight and Thermal Analysis of 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)



-Ar-	Target M_n	M_n (K)⁺ (avg.)	M.W.D.	T_g (°C)*	TGA (°C)**
BPADA	1:1	11.2	1.8	313	431
6FDA	1:1	31.7	2.0	>350	472

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 10°C/min

** in air, 10°C/min

the gas with the membrane. Gases traverse the membrane at different rates based on these two parameters. The gas pair investigated in this research was oxygen/nitrogen (O_2/N_2), which each have kinetic diameters of 3.46Å and 3.64Å, respectively. For this gas pair, the dominating factor for the rate of gas permeation is the diffusion coefficient. Since the diffusion coefficient is highly dependent on the mobility of gas through the free-volume and the free-volume distribution of the semipermeable membrane, it remains a challenge to increase the permeation rate of one species, while essentially holding the permeation rate of the other constant.

Membranes, which display both a high permeability and high selectivity toward gases, are desirable. A polymer with combined permeability and selectivity properties above the upper bound²³¹ (discussed in section 2.4.3.4) is rare. The data in this research will be referenced to the upper bound.

One approach to yield highly permeable and yet highly selective membranes is to utilize monomers which increase interchain spacing while simultaneously maintaining a rigid backbone.²³³⁻²³⁶ One such application of this method is discussed in section 2.5.1.

The approach taken in this research was to incorporate either diamines or dianhydrides which are both rigid and bulky. Monomer rigidity and bulkiness will translate into a polymer backbone which is also rigid and bulky. The bulky moieties will sterically hinder polymer-polymer interactions and serve to increase interchain spacing.

4.3.1 Permselective Behavior of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides

Diaminophenylindane is a diamine which satisfies the rigid and bulky requirements for improving gas permselectivity (Figure 4.2.1.1). The three dimensional projection clearly shows the planarity and inherent rigidity of the parent indane structure. Out from this plane are four bulky groups which cause an increased spacing between adjacent polymer chains. Three of the groups are methyls and the other is the pendant phenyl ring which bears the amine. The 3-D projection also shows the kinked structure of this monomer centered about the carbon bridging the indane structure and the phenyl

ring. The semi-rigid kink and bulky substituents will frustrate close packing between polymer chains and increase the gas permeability through thin polymer films of this material.

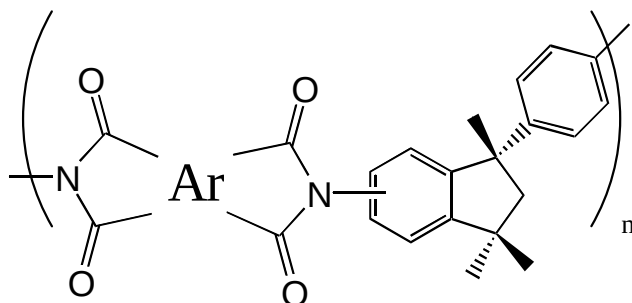
Oxygen permeability and O_2/N_2 selectivity for the homopolyimides containing DAPI are provided in Table 4.3.1.1. The first two entries, PMDA and BPDA, are considered rigid dianhydrides. Rigid repeat units may have the ability to pack well with each other and decrease the gas permeation rate. Based on this interpretation alone, PMDA, which has the greatest rigidity, should conceivably yield a thin film which has the lowest permeability when compared to the other, more flexible, dianhydrides. However, the thin film of PMDA/DAPI has the highest permeability. By changing the dianhydride to BPDA, a less rigid monomer, the oxygen permeability decreases from 34.6Ba to 5.8Ba. Although BPDA is not as rigid as PMDA, because it is a higher molecular weight semi-rigid dianhydride, it contributes a greater amount of its character to the repeat unit. Therefore, in the case of PMDA/DAPI it appears that the bulky, kinked nature of DAPI dominates the gas permeation characteristics of the thin film, i.e., allows gases to permeate rapidly which may be attributable to an increase in free volume.

A selectivity comparison between PMDA/DAPI and BPDA/DAPI reveals the less permeable polymer, BPDA/DAPI, also has the greater selectivity. This is in agreement with the inverse relationship between permeability and selectivity that has been commonly observed in gas permeation science.²³²

The gas permeation characteristics of BPADA/DAPI reveal a continued decrease in oxygen permeability and a concomitant increase in O_2/N_2 selectivity. Perhaps with this combination of monomers the more flexible dianhydride allows for more tightly packed conformations to be achieved. The polyimide BTDA/DAPI displayed a good combination of O_2 permeability and O_2/N_2 selectivity, 2.8Ba and 7.3, respectively. This polyimide may have commercial utility due to its good combination of permeability and selectivity values.

The permselectivity behavior of DAPI containing homopolyimides is plotted in Figure 4.3.1.1 against the upper bound.

Table 4.3.1.1 Oxygen Permeability and Oxygen/Nitrogen Selectivity Values for 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides

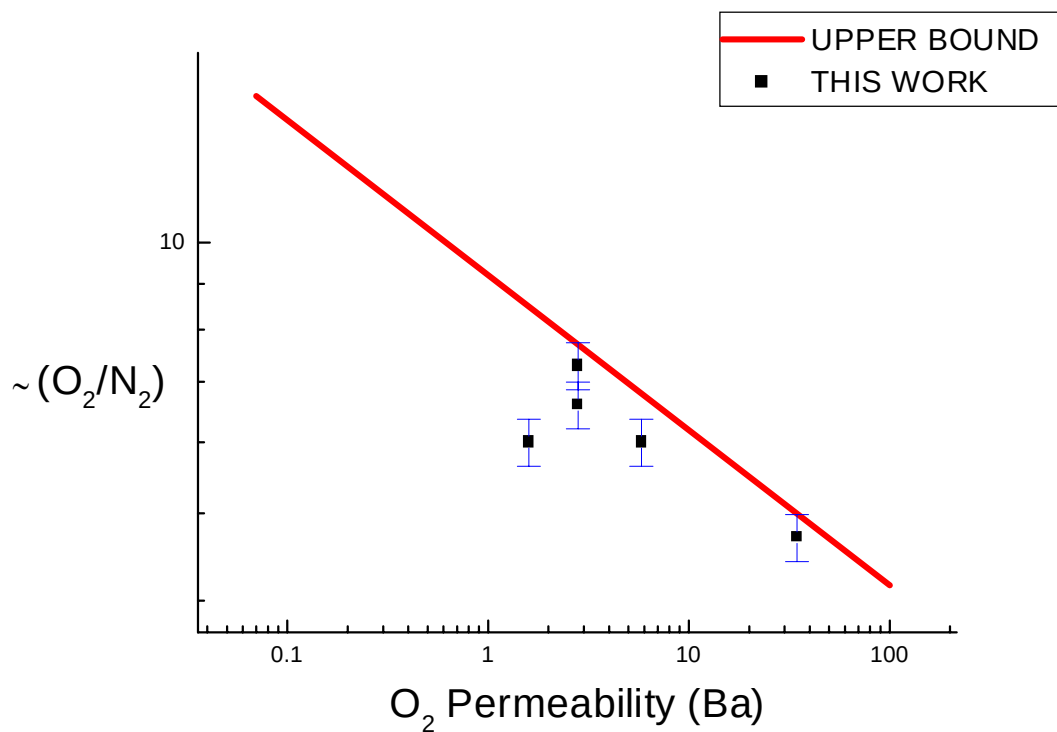


Dianhydride	O ₂ Perm. (Ba)*	O ₂ /N ₂ Selectivity**
PMDA	34.6	4.7
BPDA	5.8	6.0
BPADA	2.8	6.6
BPEDA	1.6	6.0
BTDA	2.8	7.3

T=30°C

* ±3% error

** ±6% error



*error bars for $\alpha(O_2/N_2)$ values in blue ($\pm 6\%$); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale ($\pm 3\%$)

Figure 4.3.1.1 Permselectivity Behavior of DAPI Containing Homopolyimides Relative to the Upper Bound

4.3.2 Effect of the DAPI Isomeric Ratio on Polymer Permeability and Selectivity

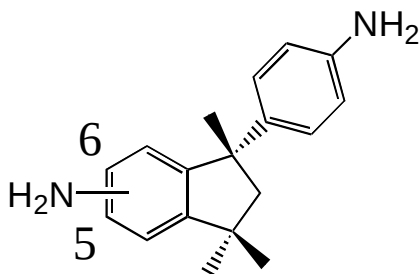
The effect of the DAPI isomeric ratio on polymer permselectivity was investigated in combination with benzophenone dianhydride (BTDA). The results of this study are presented in Table 4.3.2.1. The difference in these results for the first two systems, i.e., 30:70 and 50:50 (6:5), are within experimental error, which is typically $\pm 4\%$. However, the 60:40 isomeric DAPI ratio with BTDA has $\sim 43\%$ increase in O_2 permeability and a decrease of $\sim 57\%$ in O_2/N_2 selectivity. Since the selectivity value dropped significantly, even though the increase in permeability was high, this polyimide would not be a good candidate for gas separation. However, further experiments are needed to verify the behavior of this polymer. The overall conclusion concerning the BTDA/DAPI systems studied thus far is that alteration of the DAPI isomeric ratio had no significant effect on the permselective properties.

4.3.3 Permselective Behavior of 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione Dianhydride (6FDA) Based Polyimides

A second monomer, which satisfies the two criteria of being bulky and rigid, is 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione dianhydride (6FDA). In Figure 4.2.6.1, the structure of 6FDA is compared with that of BPDA. The bulky structure of the two $-CF_3$ groups of 6FDA and its kinked structure would hinder close packing between adjacent polymer chains. This monomer is also rigid due to steric hinderance between fluorine atoms and aromatic protons ortho to the hexafluoroisopropylidene linkage, which restricts free rotation about the $(CF_3)_2C-C(Ar)$ bond. In addition, 6FDA is known to impart solubility to polyimides.

The permselectivity values of polyimides derived from 6FDA are given in Table 4.3.3.1. The polyimide *m*-PDA/6FDA has both a relatively low O_2 permeability and O_2/N_2 selectivity. By replacing the diamine with FDA, the O_2 permeability increases by more than five fold. Both of the diamines, *m*-PDA and FDA, are quite rigid. However,

Table 4.3.2.1 Isomeric Ratio Effect on 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)/3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)
Oxygen Permeability and Oxygen/Nitrogen Selectivity Values

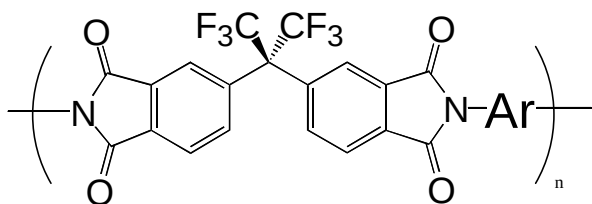


6:5 Isomeric Ratio	O ₂ Perm. (Ba)	O ₂ /N ₂ Selectivity
30:70	2.5	7.0
50:50	2.8	7.4
60:40	4.0	4.7
T=30°C		

* ±3% error

** ±6% error

Table 4.3.3.1 Oxygen Permeability and Oxygen/Nitrogen Selectivity Values for 6FDA Based Polyimides



-Ar-	O ₂ Perm. (Ba)	O ₂ /N ₂ Selectivity
m-PDA	3.0	5.5
FDA	15.3	5.8
DDBT	22.2	6.1

T=30°C

* ±3% error

** ±6% error

the difference in bulkiness is quite large. The very bulky FDA significantly increases the O₂ permeability due to its ability to impart a more open polymer conformation. Surprisingly, the O₂/N₂ selectivity for this system also increases slightly over that of *m*-PDA/6FDA.

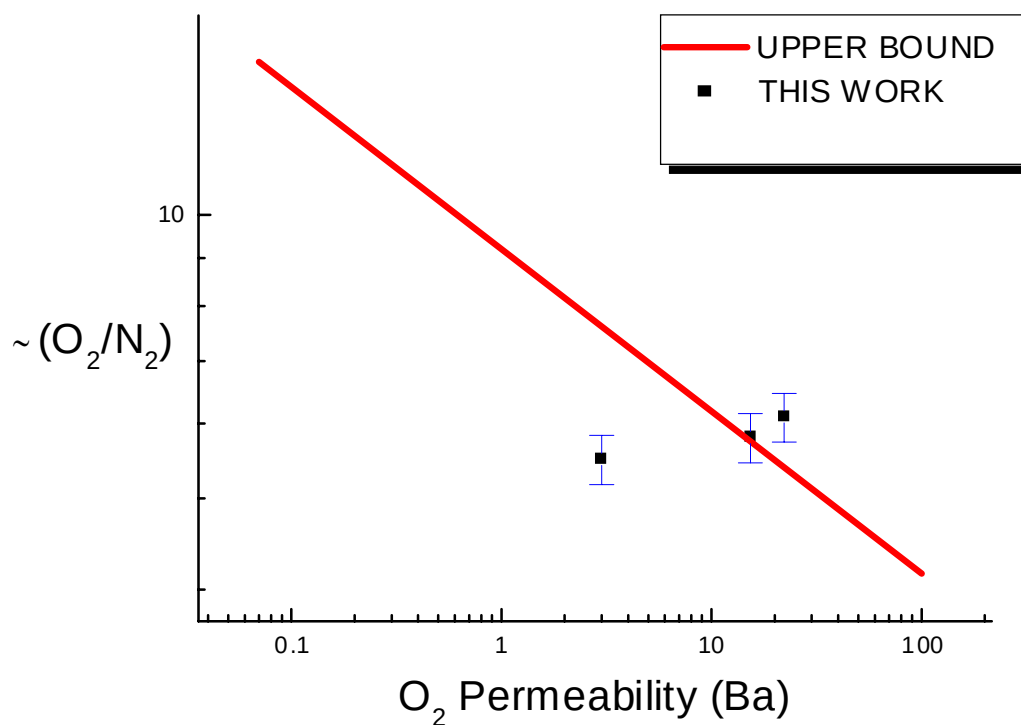
The polyimide containing the diamine, 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT), in combination with 6FDA shows an increase in O₂ permeability and O₂/N₂ selectivity over FDA/6FDA (Table 4.3.3.1). The marked increase in both permeability and selectivity is rarely observed in polymer science. The rigid structure of DDBT and its slightly bulky groups (methyl and SO₂) in combination with the possible electronic interactions of SO₂ groups are thought to impart these gas permeation characteristics. The permselectivity properties of this polymer, as well as those of the other DDBT-based polyimides, are plotted in relation to the upper bound in Figure 4.3.3.1.

4.3.4 Polymer Permeability and Selectivity of Polyimides Derived from 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)

The sulfone linked diamine, DDBT, was shown in the previous section to give high O₂ permeability and moderate selectivity values. This diamine was also condensed with BPADA and tested for its gas permselectivity behavior. In contrast to 6FDA/DDBT, BPADA/DDBT has lower O₂ permeability and O₂/N₂ selectivity values (Table 4.3.4.1). The more flexible BPADA presumably allows the polymer chains to “seek-out” a tighter conformation, which reduces O₂ permeability.

4.4 Molecular Weight and Thermal Characterization of Polyimides Containing Hydroxyl Moieties

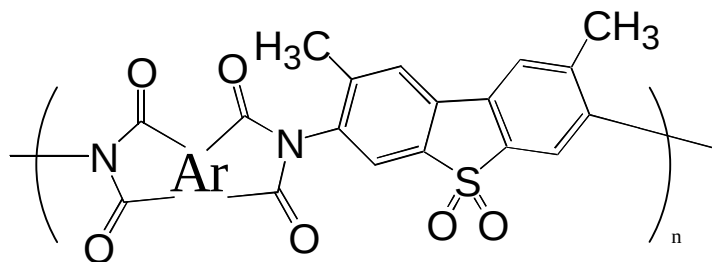
One of the objectives of this research was to investigate polyimide systems which contain hydroxyl moieties in the repeat unit. Once these materials were successfully synthesized, the influence of hydroxyl groups on thermal properties and permeability



*error bars for $\alpha(O_2/N_2)$ values in blue ($\pm 6\%$); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale ($\pm 3\%$)

Figure 4.3.3.1 Permselectivity Behavior of 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzene-furandione (6FDA)-Containing Homopolyimides as Compared to the Upper Bound

Table 4.3.4.1 Oxygen Permeability and Oxygen/Nitrogen Selectivity Values for 3,7-Diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT) Based Polyimides



	O ₂ Perm. (Ba)	O ₂ /N ₂ Selectivity
Diamine BPADA	1.9	5.5
6FDA	22.1	6.1

T=30C

* ±3% error

** ±6% error

behavior was measured. The impetus for designing such systems was based on the hypothesis that hydrogen bonding may increase chain rigidity and favorably influence gas selectivity (Figure 4.4.1).²⁴⁹

Introducing a hydroxyl group into the backbone of a polyimide may easily be accomplished by using a monomeric diamine as the carrier. Three different diamines were investigated and have been presented in the following sections.

4.4.1 Characterization of Polyimides Containing 4,4'-diamino-3,3'-dihydroxybenzidine (HAB)

Polyimides derived from HAB were expected to yield soluble polymers with the proper dianhydrides. Due to the inherently rigid structure of HAB, flexible dianhydrides were chosen to promote solubility. These were: BPADA, DSDA and 6FDA.

Polyimides incorporating HAB were synthesized by high temperature solution imidization techniques. Each of the polyimides remained soluble in the reaction solvent (NMP) even after being cooled to ~60°C before precipitating the polymer in methanol. Molecular weight and thermal characteristics of these systems are shown in Table 4.4.1.1. HAB in combination with BPADA, a more flexible dianhydride, was soluble in the reaction solution but did not dissolve in hot NMP once it had been precipitated and attempts were made to redissolve it. Therefore, molecular weight characterization of the polyimide was not possible for this system. The insolubility of HAB/BPADA was most likely due to a combination of diamine rigidity and strong intermolecular hydrogen bonding which prevents polymer redissolution.

In order to obtain a soluble system, a comonomer, DSDA, was utilized with HAB. High molecular weight polymer was achieved for this system, as determined by GPC. The molecular weight distribution of 3.3 was a little higher than the expected value of 2.0. Even though the GPC method operates under dilute solution conditions, it may have been possible in this case that the strong hydrogen bond association between chains was not sufficiently disrupted by the NMP mobile phase. Insolubility due to light crosslinking, i.e., ester formation, may also be possible. The glass transition temperature

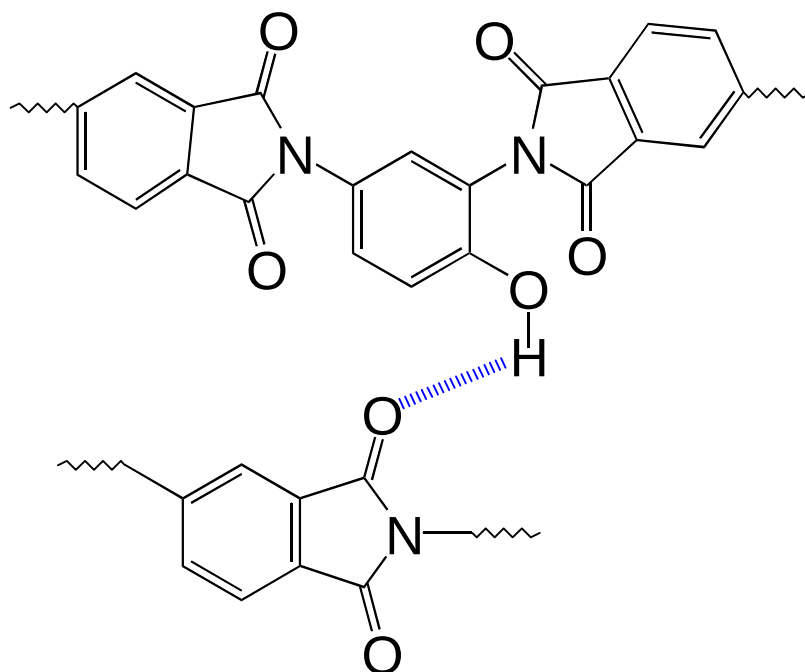
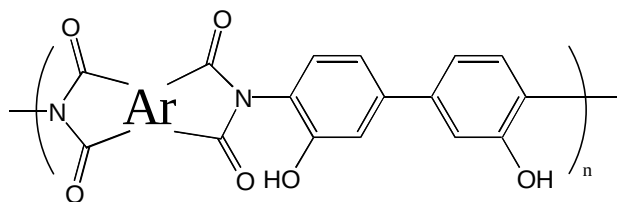


Figure 4.4.1 One Possible Type of Hydrogen Bonding in Polyimides which Contain Hydroxyl Moieties in the Backbone

Table 4.4.1.1 Molecular Weight and Thermal Analysis of 4,4'-diamino-3,3'-dihydroxybenzidine (HAB)



Dianhydride	Target M _n	M _n (K) ⁺ (avg.)	M.W.D.	T _g (°C)*	TGA (°C)**
BPADA	1:1	insol.	---	287	419
BPADA:DSDA(1:1)	1:1	83.8	3.3	---	428
6FDA	1:1	42.1	4.6	314	458

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 20°C/min

** in air; heating rate of 10°C/min

for BPADA:DSDA(1:1)/HAB was undetectable. The FTIR spectrum of a thin film showed the absorption bands typical for polyimides, as well as a broad absorption due to the phenolic -OH ($\sim 3400\text{cm}^{-1}$) (Figure 4.4.1.1).

The polymer of HAB/6FDA had high molecular weight and was soluble when redissolving the precipitate in NMP to prepare a solution. This system also had a higher molecular weight distribution than was expected. By replacing BPADA with 6FDA in the HAB-based polyimides, the T_g increased by 27°C resulting from the more rigid hexafluoroisopropylidene linkage. FTIR analysis of this polymer showed absorptions typical for polyimides (Figure 4.4.1.2).

Figure 4.4.1.3 shows percent water sorption versus time under two different conditions. Under atmospheric humidity ($\sim 50\%$) 6FDA/HAB absorbs ~ 4 weight % water after eight days. However, after being totally immersed in water for eight days the film showed >7 weight % water absorption. A typical commercial polyimide, such as Kapton, will absorb 2-3 weight % water under atmospheric conditions. The increase in water absorption for 6FDA/HAB is attributable to an increase in the hydrophilic nature of the polymer backbone due to the hydroxyl groups.

Thermogravimetric analysis of polyimides containing HAB indicates a 5% weight loss well below 500°C . Premature degradation results from the more oxidatively unstable phenol moieties.

All of these polymers yielded tough, creasable films when cast from NMP. Films of HAB/BPADA were cast from the reaction solution due to the fact that the polyimide could not be redissolved once it had been precipitated.

4.4.2 Polyimides Derived from 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF)

In view of the spurious molecular weight distributions found for HAB containing polyimides, Bis-AP-AF, a more flexible diamine containing hydroxyl groups, was introduced in an effort to reduce intermolecular chain association. Polyimides based on Bis-AP-AF were synthesized via high temperature solution imidization methods in NMP.

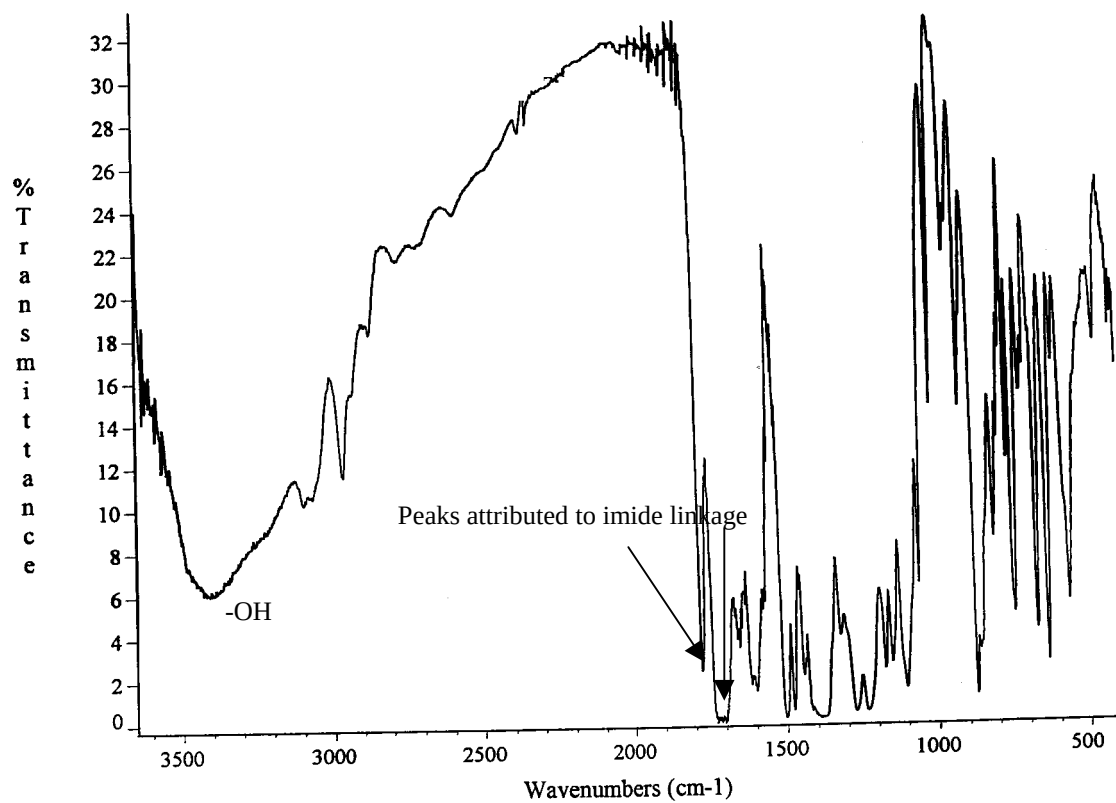


Figure 4.4.1.1 FTIR Spectrum of BPADA:DSDA(1:1)/HAB

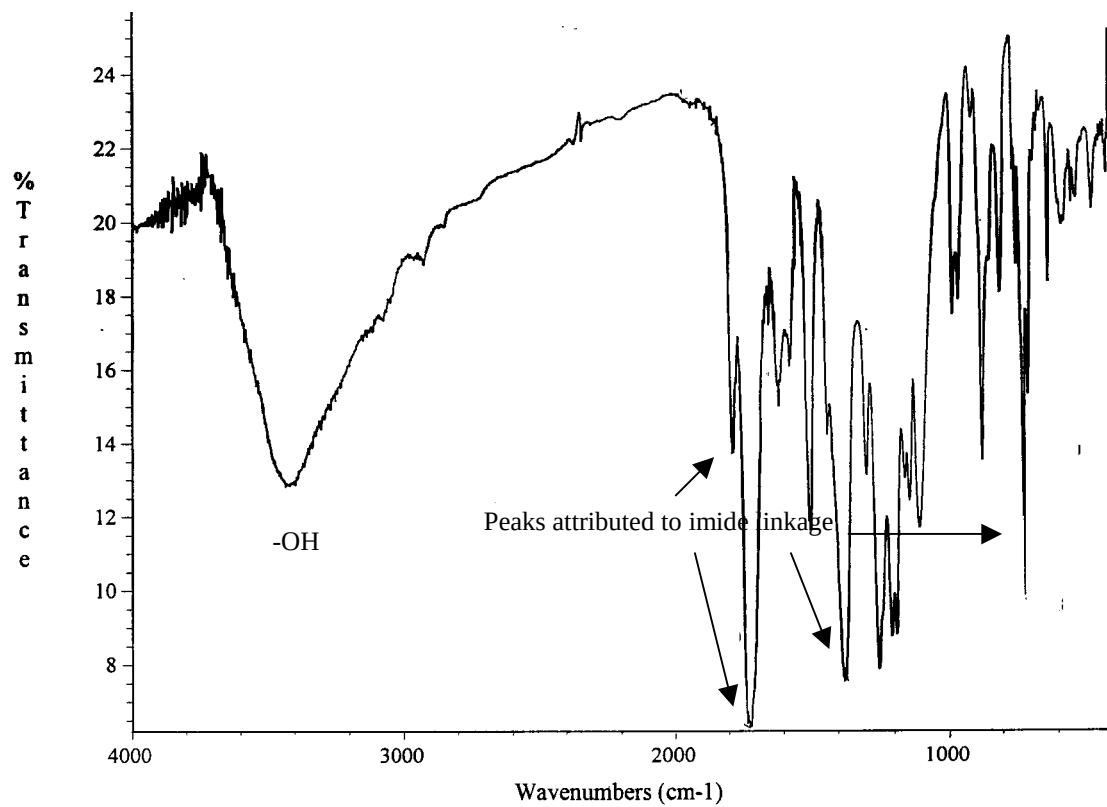
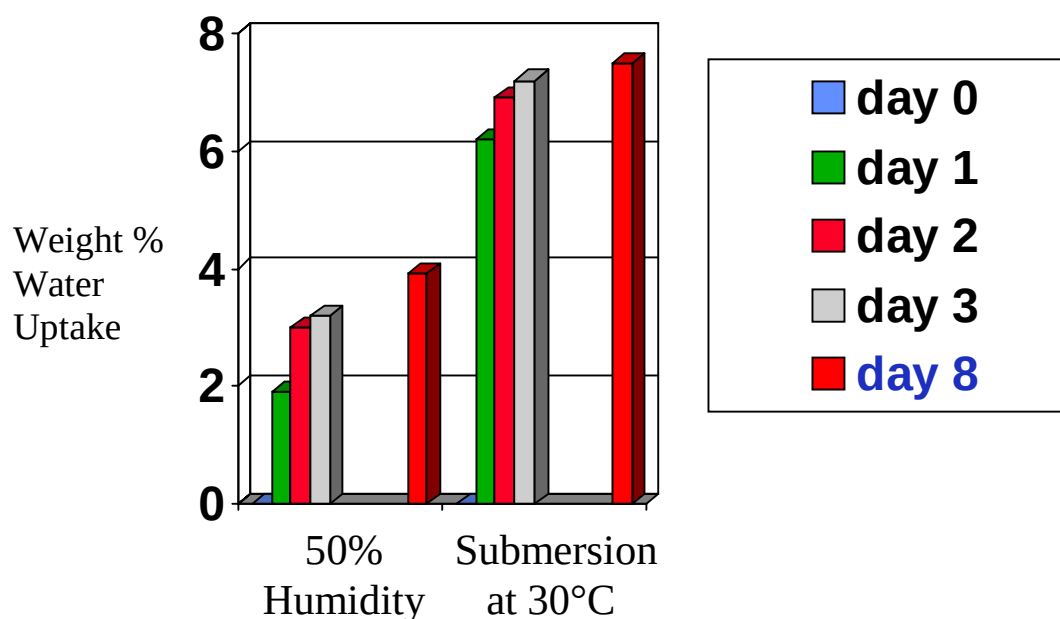
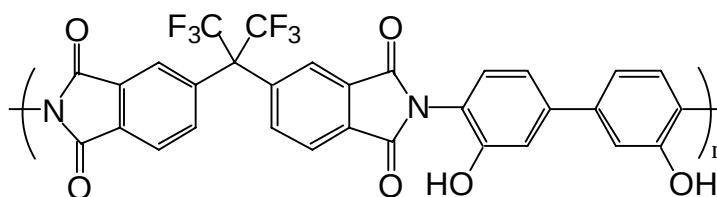


Figure 4.4.1.2 FTIR Spectrum of 6FDA/HAB



* initial film was 70 μ m thick

** 250°C under vacuum for 3 days was needed to remove trace amounts of water

*** control: Kapton polyimides typically uptake ~2-3 wt% water under atmospheric conditions

Figure 4.4.1.3 Percent Water Sorption Versus Time for 6FDA/HAB

Prior to precipitation, tough, creasable films were cast from the reaction solutions. The precipitated polymers were fibrous and insoluble in hot NMP, which was most likely due to a large degree of hydrogen bonding.

It was only possible to obtain the glass transition temperature for one of these materials because of an overlap between the T_g and polymer decomposition (Table 4.4.2.1). Figure 4.4.2.1 compares the T_g of Bis-AP-AF/BPADA with that of Bis-AT-AF/BPADA which has a similar backbone. A T_g increase of 28°C has been observed for Bis-AP-AF/BPADA over Bis-AT-AF/BPADA and can be attributed to intermolecular hydrogen bonding which decreases chain mobility. The thin film FTIR spectrum of Bis-AP-AF/BPADA shows absorption bands typical for polyimides as well as a broad absorption due to the phenolic -OH ($\sim 3400\text{cm}^{-1}$) (Figure 4.4.2.2).

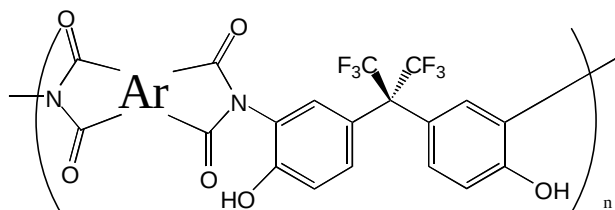
4.4.3 Polyimides Based on 2,4-Diaminophenol (DAP)

Synthetic incorporation of DAP was conducted in an attempt to arrive at soluble polyimides which contain hydroxyl groups. Unlike the two previously described diamines, HAB and Bis-AP-AF, the DAP monomer contains only one hydroxyl group. A decrease in the number of hydroxyls per repeat unit was projected to decrease the degree of hydrogen bonding and, if present, reduce crosslinking, which may lead to a more soluble systems.

Diaminophenol (DAP) was condensed with BPADA, 6FDA, BTDA and DSDA using high temperature solution imidization techniques. Molecular weight characterization and thermal behavior of these systems is provided in Table 4.4.3.1. The two soluble polyimides, DAP/BPADA and DAP/6FDA, were of high molecular weight as determined by GPC (DAP/BPADA-Figure 4.4.3.1). They also formed tough, creasable films which gave infrared absorptions typically found for polyimides, as well as a single broad peak due to the phenolic -OH ($\sim 3400\text{cm}^{-1}$) (Figure 4.4.3.2). The molecular weight distribution, as expected, was around 2.0.

The homopolyimides of DSDA and BTDA were soluble in the reaction solution. Once precipitated, however, they could not be redissolved in hot NMP. This

Table 4.4.2.1 Molecular Weight and Thermal Analysis of 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF)



Dianhydride	Target M _n	M _n (K) ⁺ (avg.)	M.W.D.	T _g (°C)*	TGA (°C)**
BPADA	1:1	insol.	---	252	415
BTDA	1:1	insol.	---	>275	448
6FDA	1:1	insol.	---	>310	403

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 20°C/min

** in air; heating rate of 10°C/min

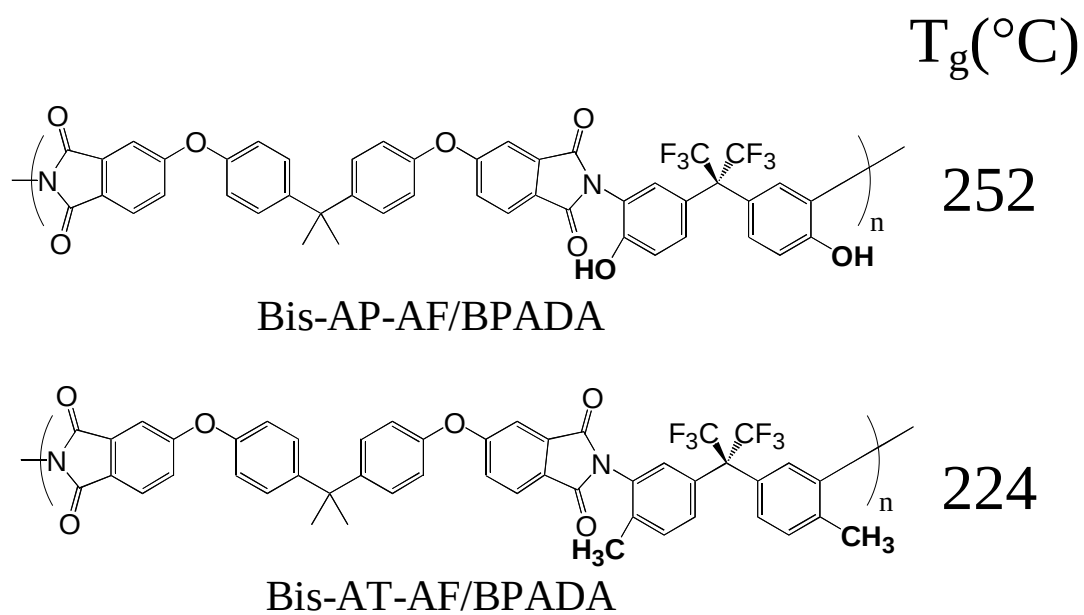


Figure 4.4.2.1 Chemical Structures and T_g of Bis-AP-AF/BPADA and Bis-AT-AF/BPADA

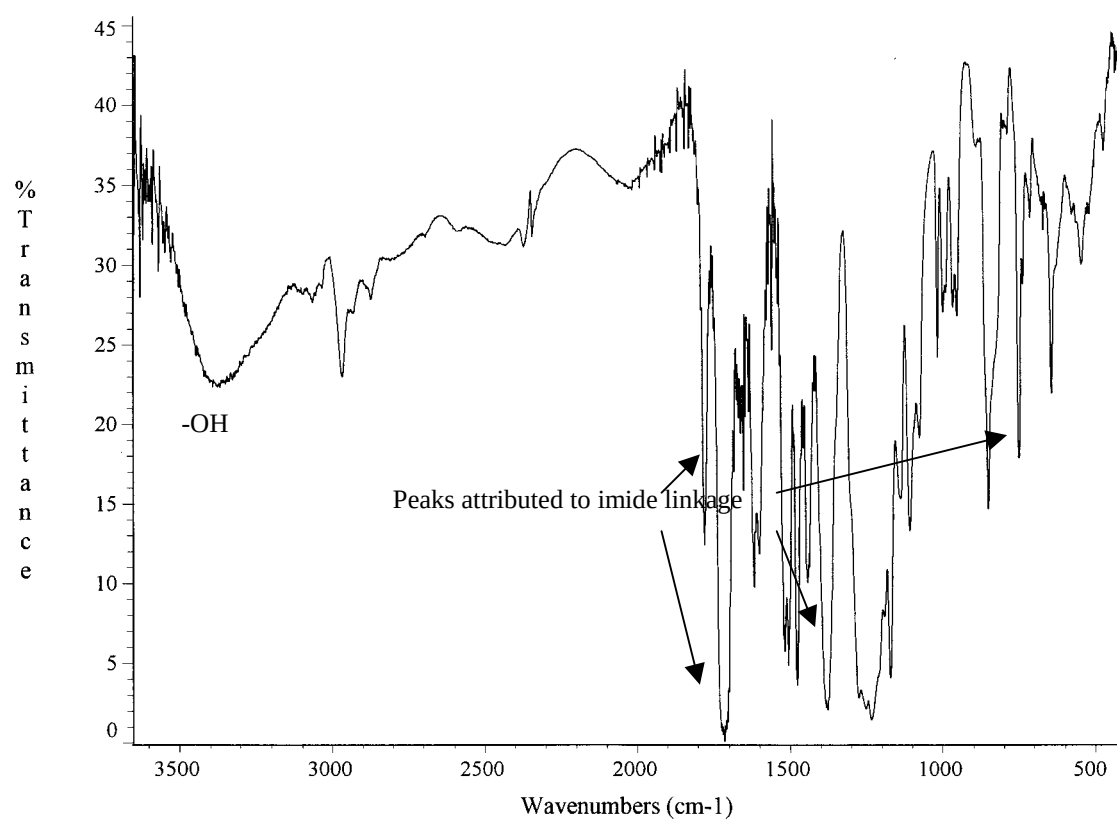
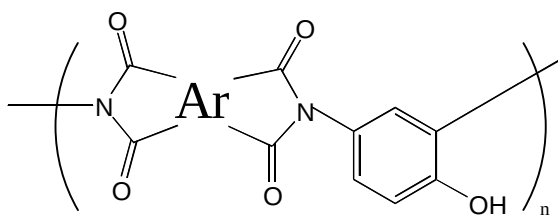


Figure 4.4.2.2 FTIR Spectrum of Bis-AP-AF/BPADA

Table 4.4.3.1 Molecular Weight and Thermal Analysis of 2,4-diaminophenol (DAP)
Based Polyimides



-Ar-	Target M_n	M_n (K)⁺ (avg.)	M.W.D.	T_g (°C)*	TGA (°C)**
BPADA	1:1	37.2	2.2	247	435
6FDA	1:1	23.0	2.0	338	450
DSDA	1:1	insol.	---	>325	480
BTDA	1:1	insol.	---	>340	435

+ via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

* 2nd heating; heating rate of 20°C/min

** in air; heating rate of 10°C/min

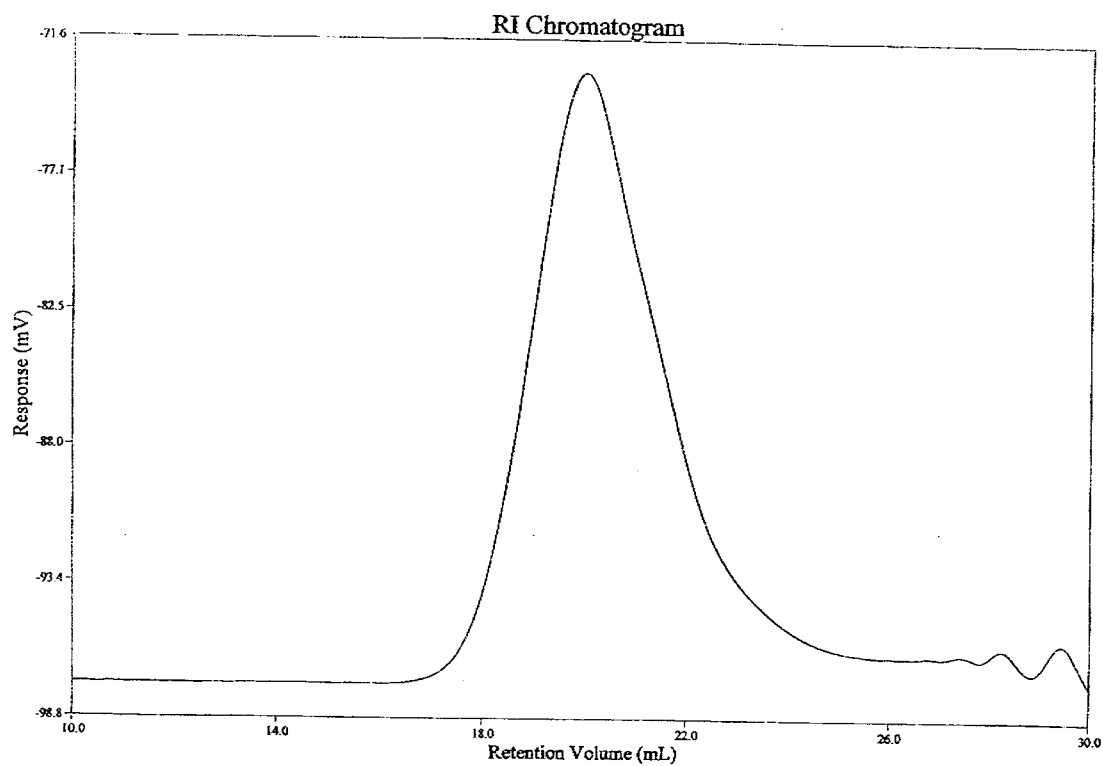


Figure 4.4.3.1 Gel Permeation Chromatogram of DAP/BPADA Based Polyimide (mobile phase was NMP + 0.02MP₂O₅, 60°C)

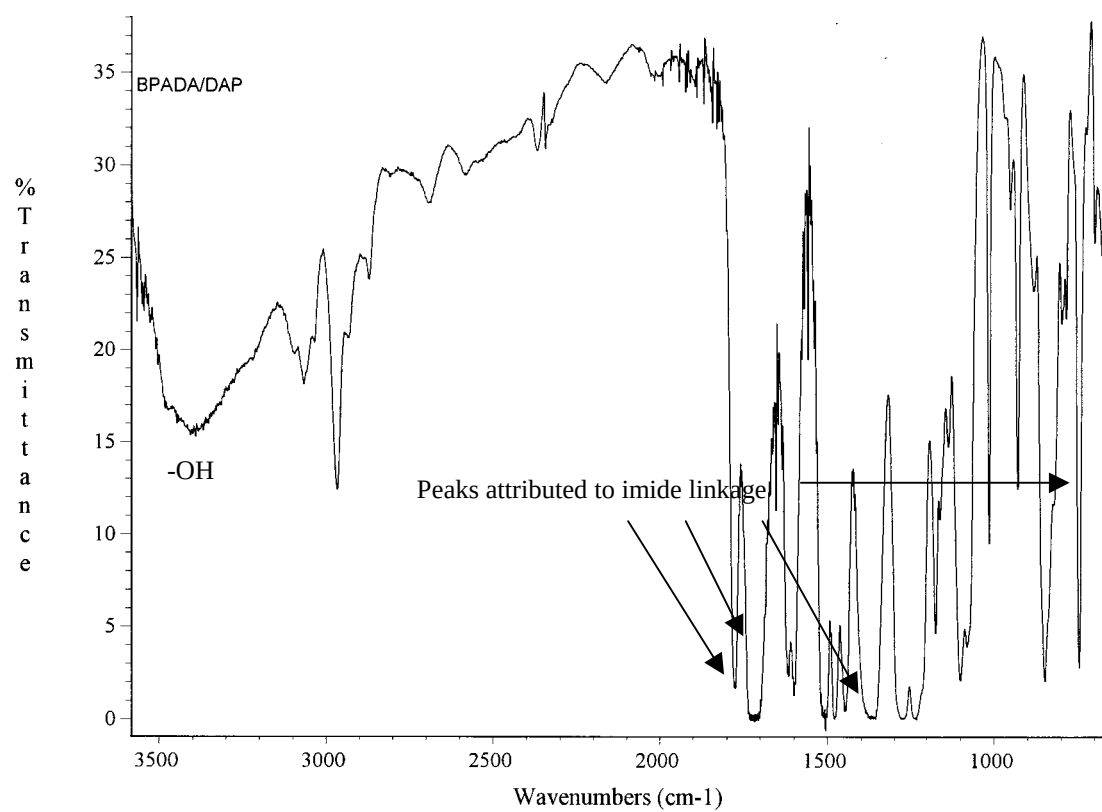


Figure 4.4.3.2 FTIR Spectrum of DAP/BPADA

phenomenon may result from a combination of strong intermolecular hydrogen bonding, light crosslinking (i.e., ester formation), and partial crystallinity, although the latter two have not been verified.

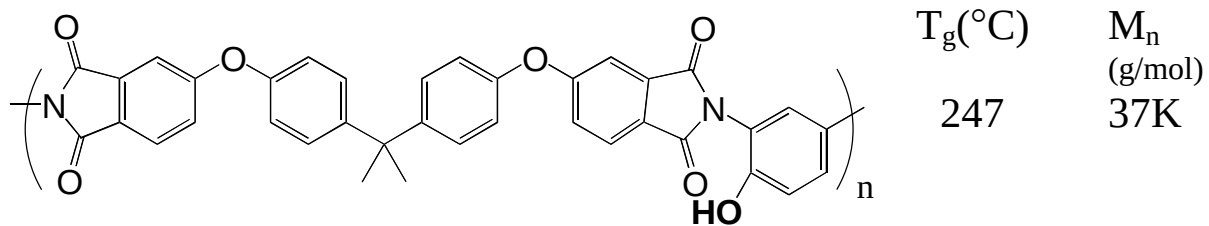
Glass transition temperatures of BPADA and 6FDA polyimides containing DAP were found to be 247°C and 338°C, respectively. Comparison of BPADA/DAP with BPADA/*m*-PDA, whose repeat unit differs by the absence of a hydroxyl group, showed the T_g to be increased by 30°C for the DAP system. Comparing 6FDA/DAP with 6FDA/*m*-PDA shows an increase in T_g of 43°C was observed (Figure 4.4.3.3) for the DAP based polyimide. In each system, the T_g has increased due to additional interaction between polymer chains through hydrogen bonding. Increasing polymer-polymer interactions via hydrogen bonding increased chain rigidity, which in-turn increased the relaxation temperature, T_g .

Determination of a glass transition temperature for DSDA/DAP and BTDA/DAP polyimides was not possible due to the transition occurring above the initial polymer degradation temperature.

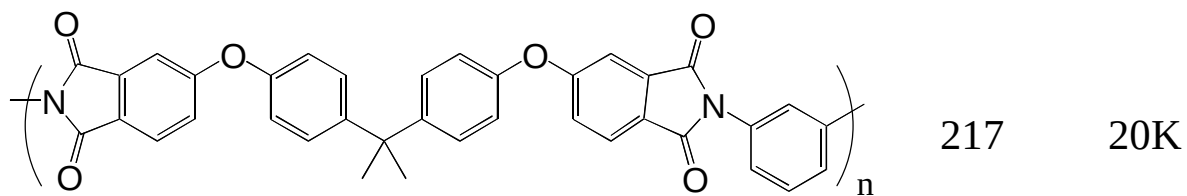
Thermogravimetric analysis in air revealed lower degradation temperatures when compared to the non-hydroxyl containing analogs. Weight loss values below 500°C resulted from the oxidatively more unstable phenolic sites.

4.5 Gas Permselectivity Studies Performed on Polyimides Containing Hydroxyl Moieties

Polyimides containing pendant phenol groups were of interest in this research for gas separation. It was hypothesized that by increasing intermolecular chain rigidity may result in an increase in gas permselectivity. Polymers containing 4,4'-diaminobiphenyl-3,3'-diol (HAB) and 2,4-diaminophenol (DAP) were tested to determine their semipermeable behavior toward gaseous O₂ and N₂.



DAP/BPADA



***m*-PDA/BPADA**

Figure 4.4.3.3 Chemical Structure and Glass Transition Temperature of 6FDA/DAP and 6FDA/*m*-PDA Based Polyimide

4.5.1 Permselective Behavior of 4,4'-diaminobiphenyl-3,3'-diol (HAB) Based Polyimides

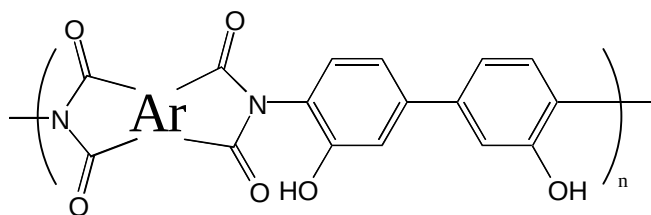
Homopolyimides based on HAB were investigated for their permselective behavior. HAB was chosen for two reasons: first, it has the ability to form intermolecular hydrogen bonds through the pendant phenol moiety and, secondly, it is a rigid diamine which facilitates a reduction in permeability.

The gas permeation values for these systems are given in Table 4.5.1.1. The BPADA/HAB system shows excellent O₂/N₂ selectivity and moderate permeability. Due to the relative insolubility of the BPADA/HAB polyimide, a soluble copolymer derived from BPADA and DSDA (50/50) was selected for comparison. DSDA, compared to BPADA, is a more rigid dianhydride and was expected to decrease O₂ permeability and increase O₂/N₂ selectivity. As shown in Table 4.5.1.1, this was indeed observed.

The hexafluoro bridge present in 6FDA is known to yield soluble systems and impart good permeability characteristics to semipermeable membranes. The 6FDA/HAB based polyimide was indeed soluble and had permeability characteristics which were quite interesting. Compared to BPADA/HAB, the 6FDA/HAB polyimide film decreases slightly in O₂/N₂ selectivity and increases greatly in O₂ permeability. The O₂/N₂ selectivity decreases by ~7% (within %error), while the O₂ permeability increases by 5 fold. As was discussed in section 4.3.3, 6FDA hinders chain packing and generally increases permeability. However, such a large increase in permeability is often accompanied by a greater decrease in O₂/N₂ selectivity, which was not found in this case. The difference in permselectivity values between BPADA/HAB and 6FDA/HAB may result from the greater phenol concentration present in 6FDA/HAB (moles OH/gram repeat unit), which may facilitate an increase in rigidity and lead to a higher selective system.

Gas permeability characteristics of polyimides based on HAB are plotted against the upper bound in Figure 4.5.1.1.

Table 4.5.1.1 Oxygen Permeability and Oxygen/Nitrogen Selectivity Values for 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) Based Polyimides

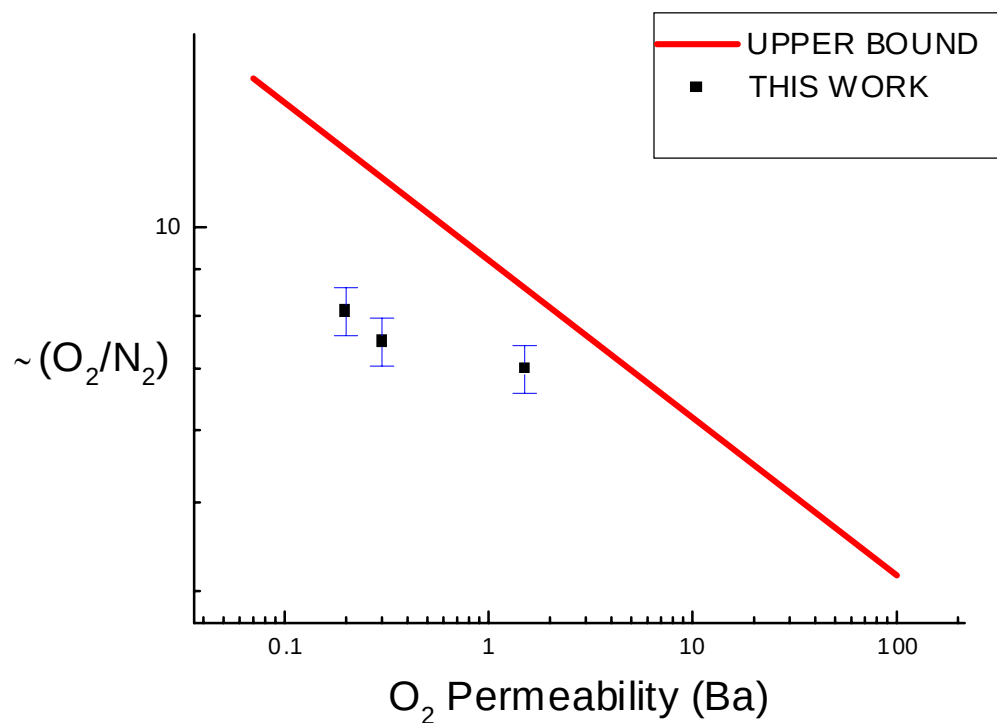


	O ₂ Perm. (Ba)	O ₂ /N ₂ Selectivity
Dianhydride BPADA	0.3	7.5
BPADA:DSDA(50:50)	0.2	8.1
6FDA	1.5	7.0

T=30°C

* ±3% error

** ±6% error



*error bars for $\alpha(O_2/N_2)$ values in blue ($\pm 6\%$); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale ($\pm 3\%$)

Figure 4.5.1.1 Permselectivity Behavior of HAB Containing Homopolyimides as Compared to the Upper Bound

4.5.2 Polymer Permeability and Selectivity of Polyimides Derived from 2,4-Diaminophenol

It was also of interest in this research to make a direct comparison between polyimide repeat units, both with and without phenolic sites. One such system was prepared and is shown in Figure 4.5.2.1. Both the O₂ permeation and O₂/N₂ selectivity values are similar to each other within experimental error ($\pm 2\%$). It is clear from the T_g data for these two systems that the polyimide containing DAP has a greater degree of intermolecular attraction (the T_g increase by $\sim 30^\circ\text{C}$). The tight polymeric structure, in this case, may be offset by the bulky phenolic moieties, which increases interchain spacing and result in the overall observation of negligible differences in permselectivity values.

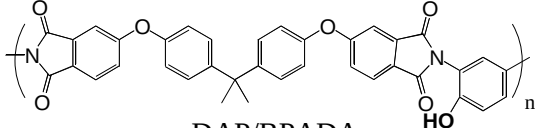
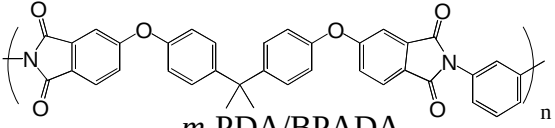
4.6 Applicable Crosslinking Mechanisms for Hollow Fiber Technology

Another objective of this research was to design and synthesize a polyimide system which could be cured at a moderately elevated temperature to yield a lightly crosslinked network. It was thought that light crosslinking might alter selectivity and permeability characteristics. Crosslinked materials have also been known to exhibit an increased resistance to solvents and contaminants, which would be an advantage for many applications.

The crosslinking reaction criteria had two important limitations: the reaction temperature must not exceed 150°C and must be completed within a time period of 2 hours. The reaction restrictions were imposed because of the need to maintain the proper polymer configuration for achieving high fluxes, i.e., hollow fibers.

Four reactive candidates were investigated. The candidates were amine-terminated, acetylene-terminated and phenol-terminated polyimides, as well as a polyimide with a pendant phenol group in the polymer repeat unit. The amine and phenol

Table 4.5.2.1 Oxygen Permeability and Oxygen/Nitrogen Selectivity Values for 2,4-diaminophenol (DAP) and 1,3-phenylenediamine (*m*-PDA) Derived Polyimides

Polymer Structure	O ₂ Perm. (Ba)	O ₂ /N ₂ Selectivity
 DAP/BPADA	0.4	8.0
 <i>m</i> -PDA/BPADA	0.5	7.8

T = 30°C

* ±3% error

** ±6% error

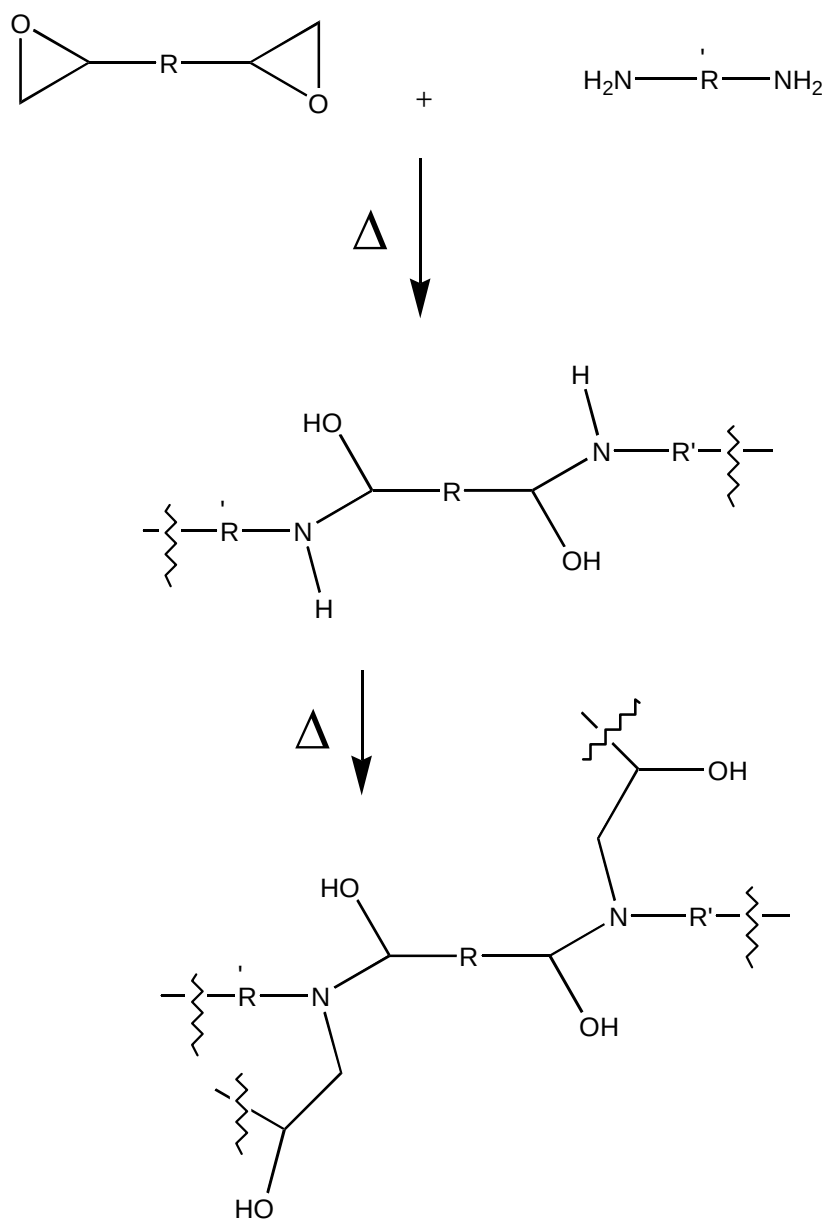
containing polyimides were reacted with epoxy and the acetylene-terminated system was reacted as a neat material. The following sections discuss how the four candidates were synthesized, characterized and evaluated for their reactivity, under the given reaction restrictions.

4.6.1 Curing Studies of Amine Terminated Oligomers with Epoxy-Cast from Chloroform

Curing of an epoxy with an amine is depicted in Scheme 4.6.1.1, which is known to undergo chain extension prior to crosslinking. A typical cure schedule for an epoxy/amine system, such as 4,4'-diaminodiphenylsulfone/Epon 828 (a difunctional epoxy), is 170°C for 1 hour prior to doing a post cure at 230°C for 30 minutes. Cure temperatures of 170°C and 230°C are required to impart sufficient molecular mobility to the system.

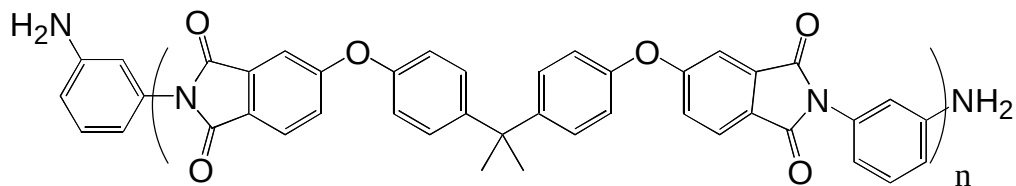
The first two systems investigated in this research were amine terminated oligomers of five and fifteen thousand grams per mol molecular weight having a backbone comprised of BPADA/*m*-PDA. The molecular weight and thermal behavior of these two polymers, which had been synthesized by the ester-acid route, are shown in Table 4.6.1.1. The T_g for these polymers was found to be 199°C and 215°C for the five and fifteen thousand grams per mol molecular weight oligomers, respectively. Curing of these two polymers must be effected, if possible, at 150°C within 2 hours. This presents quite a challenge considering the cure temperature is ~50°C below T_g .

The amine terminated oligomer based on BPADA/*m*-PDA oligomer of ~15,000g/mol was cured using a difunctional epoxy, Epon 828. The endgroup titration values obtained for the polyimide oligomer and epoxy were used to calculate a 1:1 mole ratio of reactive groups (1 amine/2 epoxide rings) for the blend. The polyimide and epoxy were then mixed together in chloroform (wt. Epoxy/ wt. Oligomer=5.2%). Bubble-free films of this reactive blend were cast from chloroform (~30wt%) dried at 100°C for 24 hours until little or no chloroform remained in the films.



Scheme 4.6.1.1 Typical Chain Extension/Curing of Epoxy Resins with Amines

Table 4.6.1.1 Molecular Weight and Thermal Characterization of Amine Terminated Oligomers



m-PDA/BPADA

Target M_n (K)	Titration		M.W.D.	T_g (°C)***
	M_n (K)* (avg.)	M_n (K)** (avg.)		
5.0	5.99	8.3	1.6	199
15.0	14.21	16.6	1.8	215

* HBr/AcOH, $\pm 1.0\%$
(multiple runs)

** via GPC, mobile phase NMP + 0.02MP₂O₅, 60°C

*** 2nd heating; heating rate of 20°C/min

Differential scanning calorimetry of a film dried at 100°C showed an initial T_g of 133°C, followed by a cure exotherm of 149°C. A second T_g for this system appeared at 189°C, followed by a second cure exotherm at 217°C (Figure 4.6.1.1). The T_g of the final cured blend was 191°C. A dynamic DSC scan was made after “curing” at 150°C for two hours in a convection oven. The system remained soluble with no molecular weight increase, and the cure exotherm occurred at 170°C in the DSC, which is well above the desired cure temperature of 150°C.

The molecular mobility in the system was increased by lowering the molecular weight of the oligomer to 5,000g/mole (Table 4.6.1.1). Moreover, the difunctional epoxy, Epon 828, was replaced with the normally tetrafunctional epoxy, MY721. An epoxy with a greater functionality may increase the likelihood of chain extension and/or crosslinking.

Following the procedure above, a five thousand gram per mol molecular weight BPADA/*m*-PDA polyimide was blended with 7.5% MY721 (1:1). Then the blend was solution cast from chloroform and was dried at 100°C under vacuum for ~24 hours before curing at 150°C for 2 hours. At the end of 2 hours curing time there were no detectable differences in the film by DSC, IR, GPC or in solubility, signifying that no reaction had occurred. This same system was taken to 210°C and periodically monitored by solubility in chloroform and GPC. Figure 4.6.1.2 shows the GPC results of this system as a function of time. Even after 15 minutes of reaction, a detectable increase in molecular weight was observed, which suggested that the crosslinking reaction occurs at this higher temperature.

4.6.2 Curing Studies of Amine, Phenol and Acetylene Containing Polymers-Cast from NMP

The previous section details the curing behavior of amine terminated polyimide oligomers cast from chloroform. In summary, the crosslinking reaction was not detected at 150°C by a number of analytical techniques. This section records the investigation of reactive oligomers cast from NMP. The higher boiling point solvent, NMP, was chosen to increase molecular mobility at the reaction temperature of 150°C. Figure 4.6.2.1

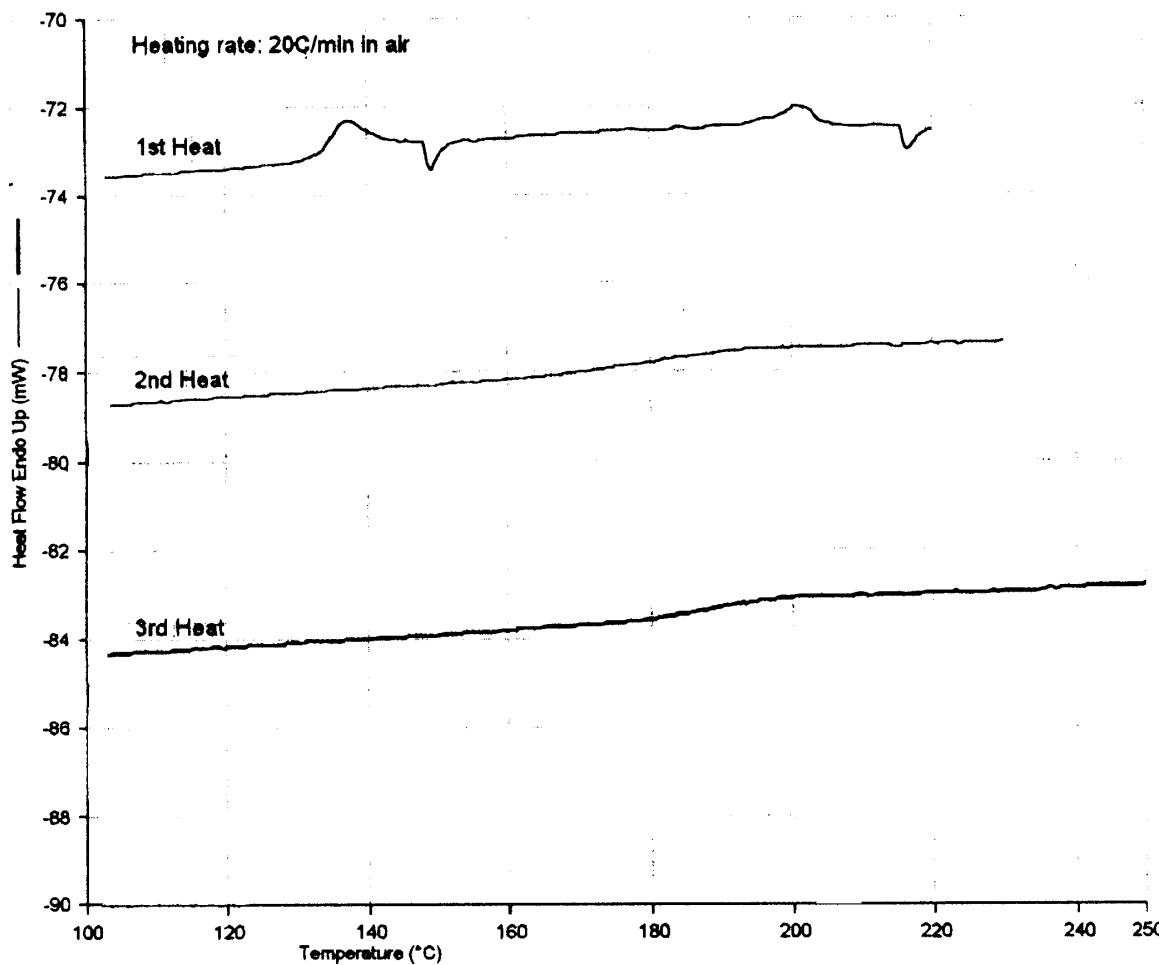


Figure 4.6.1.1 DSC Thermogram of 15kg/mole Amine Terminated Polyimide with Epon 828

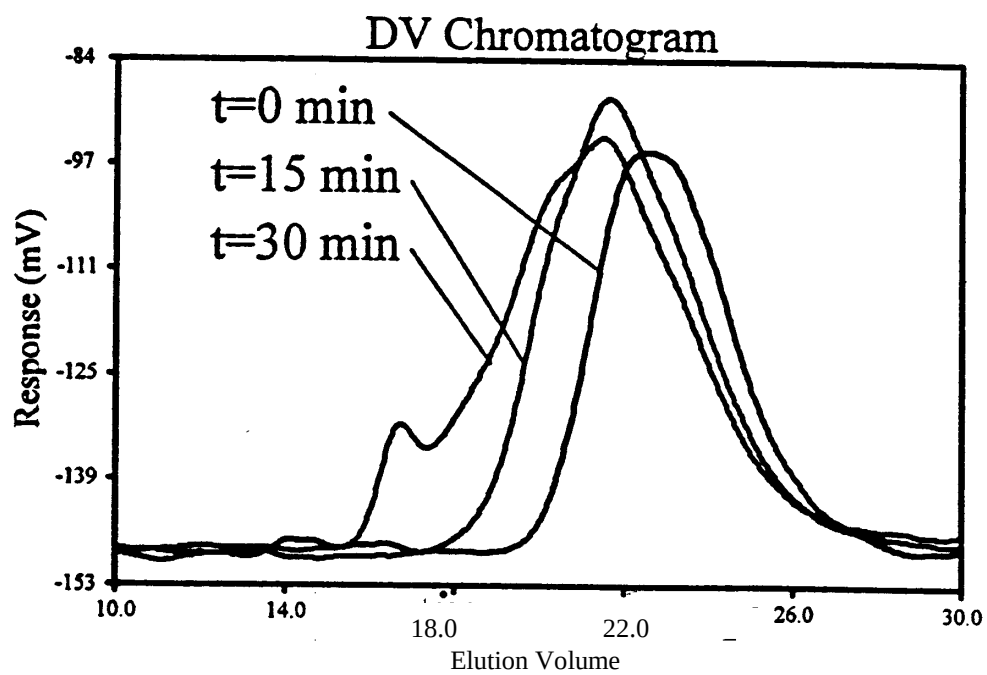
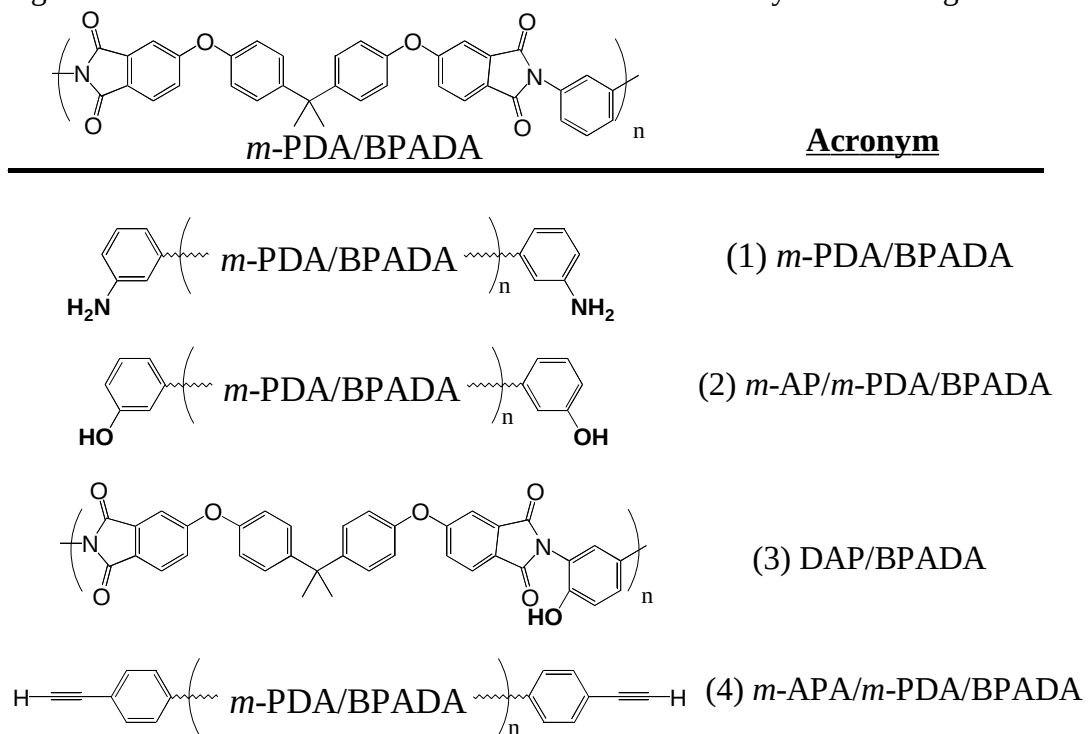


Figure 4.6.1.2 Elution Volume as a Function of Cure Time at 210°C (mobile phase was NMP + 0.02MP₂O₅, 60°C)

Figure 4.6.2.1 Chemical Structures of the Four Reactive Polymers Investigated



depicts the chemical structure of the four polymers investigated. Each of these polymers were synthesized via the ester-acid route except BPADA/DAP, which was synthesized by high temperature solution imidization methods. Molecular weight and thermal characterization, as well as titration values, are shown in Table 4.6.2.1.

Three of the four polymers were blended with epoxy (MY721), $f=4$. These were: BPADA/*m*-PDA (7.3wt% epoxy), BPADA/*m*-PDA/*m*-AP (4.5wt% epoxy) and BPADA/DAP (1.2wt% epoxy) (Table 4.6.2.2). A catalyst, triphenylphosphine, was also added to the two polymers which contained pendant phenol moieties.

Triphenylphosphine catalyzes epoxy/phenol reactions by nucleophilic addition to the epoxidized ring, followed by proton transfer and S_N2 displacement by the phenoxide anion. The acetylene terminated oligomer was cured without epoxy or catalyst. The four polymer systems were solution cast from NMP (15wt%) and dried at 100°C under vacuum for 12 hours and were estimated to contain ~5-15wt% residual NMP.

The curing reaction of these systems at 150°C was monitored as a function of time by GPC. For the amine and acetylene terminated oligomers, no molecular weight increase was observed within a 2 hour time period. However, for the catalyzed phenol terminated oligomer, as well as for the catalyzed high molecular weight polyimide with phenolic sites in the repeat unit, molecular weight increase was found by GPC. Figures 4.6.2.2 and 4.6.2.3 show the GPC traces of these two thermosetting systems as a function of time. The phenol terminated oligomer undergoes a chain extension reaction after 120 minutes (Figure 4.6.2.2). The polymer with the phenol moieties in the repeat unit reacts within 15 minutes, beyond which time it becomes insoluble (Figure 4.6.2.3).

Clarification is needed regarding the factors leading to the observed crosslinking reaction which takes place 100°C below the T_g of these materials. It is thought that the presence of both a higher boiling point solvent and the epoxy resin facilitates sufficient molecular mobility in the system to allow a chemical reaction to occur. The nature of this crosslinking mechanism can be optimized and controlled by a number of variables such as the concentration of the phenolic moiety, catalyst and epoxy, as well as residual NMP content. The effects of crosslinking on the permselectivity of these films is suggested for future study.

Table 4.6.2.1 Molecular Weight and Thermal Characterization of Functional Polyimides

Polyimide	Target M _n (K)	Titration		M.W.D.	T _g (°C)***
		M _n (K)* (avg.)	M _n (K)** (avg.)		
<i>m</i> -PDA/BPADA	5.0	5.99	8.3	1.6	199
<i>m</i> -AP/ <i>m</i> -PDA/BPADA	5.0	6.0 [∇]	6.7	---	---
DAP/BPADA	1:1	---	37.2	2.2	247
<i>m</i> -APA/ <i>m</i> -PDA/BPADA	5.0	5.1 ^{∇∇}	4.9	1.5	191

* HBr/AcOH, ±1.0% (multiple runs)

** via GPC, mobile phase was NMP + 0.02MP₂O₅, 60°C

*** 2nd heating; heating rate of 20°C/min

∇ via ¹³C NMR

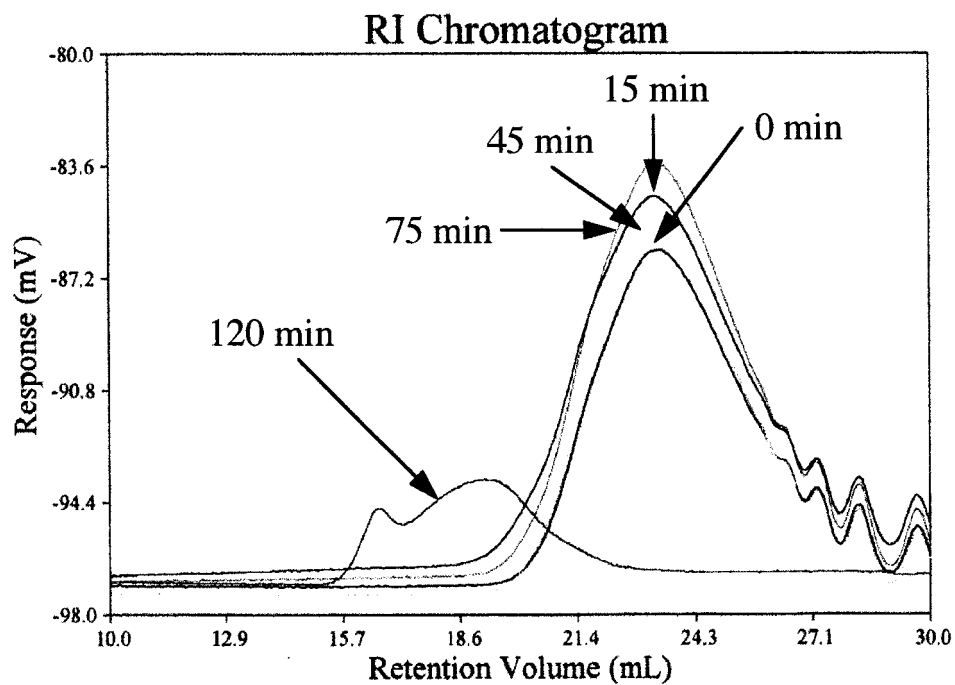
∇∇ via ¹H NMR

Table 4.6.2.2 Cure System Compositions

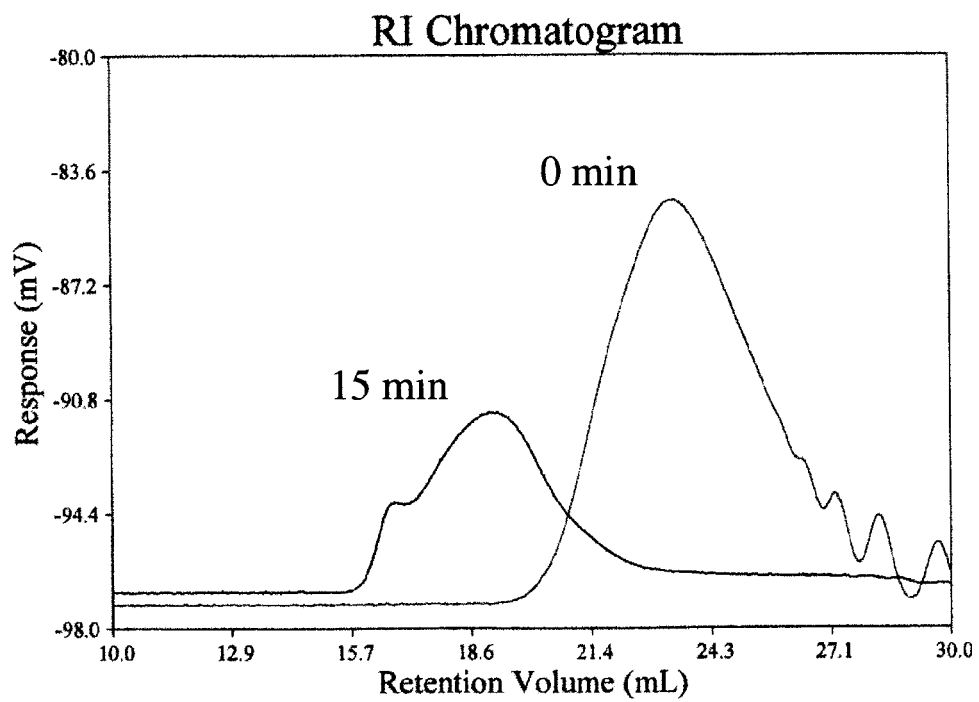
Polyimide	Epoxy Conc.(wt%) (MY721)	Catalyst Conc.(wt%)* (TPP**)
<i>m</i>-PDA(offset)/BPADA (amine term.), ~5K	7.3 (N-H/epoxy ring) (1:1)	---
<i>m</i>-AP/<i>m</i>-PDA/BPADA (phenol term.), ~5K	4.5 (O-H/epoxy ring) (1:1)	0.5
DAP/BPADA (1/1), ~37K	1.2 (O-H/epoxy ring) (~300:1)	0.8
<i>m</i>-APA/<i>m</i>-PDA/BPADA (acetylene term.), ~5K	---	---

* based on epoxy wt%

** triphenylphosphine



Figures 4.6.2.2 GPC Chromatograms of 5kg/mole Phenol Terminated Polyimide Cured at 150°C with MY721 (mobile phase was NMP + 0.02MP₂O₅, 60°C)



* insoluble after 15 min

Figures 4.6.2.3 GPC Chromatograms of 37kg/mole BPADA/DAP Cured at 150°C with MY721 (mobile phase was NMP + 0.02MP₂O₅, 60°C)

CHAPTER 5 CONCLUSIONS

The principle goal of this research was the synthesis and characterization of high molecular weight, soluble polyimide gas separation membranes. A method was also developed for lightly crosslinking phenol/epoxy systems.

The monomers, diaminophenylindane (DAPI), triaminophenylindane (TAPI) and dihydroxyphenylindane (DHPI), were synthesized and characterized by a number of analytical techniques.

The ester-acid high temperature solution imidization route was utilized to form high molecular weight polyimides of DAPI in combination with a number of commercially available dianhydrides. The isomeric, asymmetric, bulky and rigid nature of DAPI imparted a number of desirable properties to these polymers, including high solubility in common organic solvents, very high glass transition temperatures and good thermal oxidative stability. In addition, the DAPI/6FDA polyimide displayed a low refractive index value due to the fluorine content furnished by 6FDA and the partial aliphatic character of DAPI. The estimated dielectric constant of this polyimide system, which was quite low, make this polymer attractive for use in the microelectronics field. Despite the aliphatic character of DAPI, the long-term stability of the DAPI/6FDA polyimide was comparable to that of a PMDA/ODA based Kapton under nitrogen at 400°C. Further studies on photoinduced crosslinking in copolyimides for microelectronics packaging are planned, following up on research initiated by Eric Moyer in our laboratory.

The rigid, bulky and isomeric structure of DAPI in the polyimide repeat unit imparted excellent film forming characteristics. Cast membranes were produced which displayed a range of O₂ permeability and O₂/N₂ selectivity characteristics. High O₂ permeabilities were observed for polyimides in which DAPI contributed a large portion of its character to the overall polymer repeat unit, i.e. in combination with low molar mass dianhydrides. The more flexible dianhydrides afforded a greater degree of molecular freedom resulting in a more tightly packed polymer conformation, which decreased the rate of gas penetration through thin films and increased the O₂/N₂ selectivity values. The

DAPI/BTDA system showed the best combination of O₂ permeability and O₂/N₂ selectivity values, which were not significantly effected by moderate changes in the isomeric ratio of DAPI.

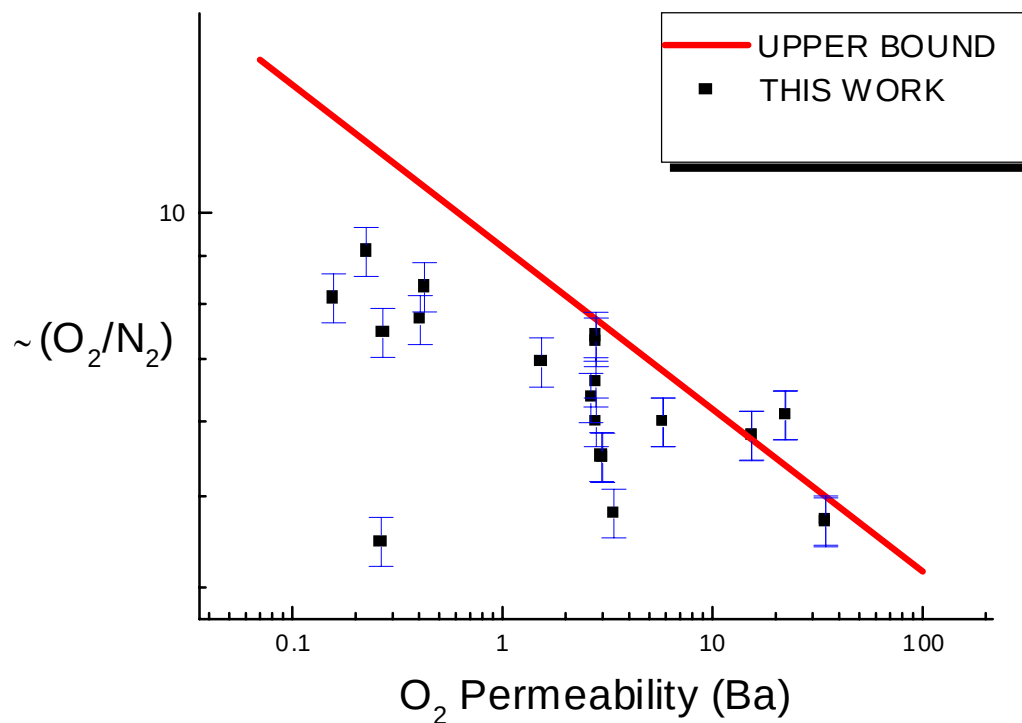
Polyimides derived from 6FDA gave high T_g, soluble systems with good thermal stability. Permselectivity values obtained from thin films of 6FDA based polyimides in combination with FDA and DDBT were excellent. These two polymers displayed a combination of O₂ permeability and O₂/N₂ selectivity values either on or above the so-called “upper bound”.

Several novel polyimides containing hydroxyl moieties were synthesized and characterized by molecular weight and thermal techniques. Due to the inherent chemical structure of the monomers coupled with a high degree of hydrogen bonding and possible side-reactions involving crosslinking, many of these were insoluble. Incorporation of hydroxyl moieties in the repeat unit was shown to enhance chain stiffness via intermolecular hydrogen bonding.

High O₂/N₂ selectivity for all of the HAB containing polymers was discovered, but was also combined with quite low O₂ permeabilities, which suggests a tightly packed structure, possibly facilitated by hydrogen bonding. Direct comparison of a polymer repeat unit with and without a hydroxyl group did not reveal a significant change in permselectivity behavior.

The O₂ permeability and O₂/N₂ selectivity values of the polyimides synthesized and characterized in this thesis are compiled in relation to the “upper bound” in Figure 5.1.

Several thermosetting systems were also designed and synthesized to lightly crosslink thin films at temperatures below the “dry” T_g of the polymer. Both the phenol terminated oligomers and the higher molecular weight phenol containing repeat unit, reacted within 2 hours at 150°C with a tetrafunctional epoxy. The crosslinking reaction occurred ~100°C below the T_g of the “dry” polymer and was thought to be facilitated by residual solvent (NMP) and epoxy content.



*error bars for $\alpha(O_2/N_2)$ values in blue ($\pm 6\%$); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale ($\pm 3\%$)

Figure 5.1 Research Summary: Permselectivity Behavior of Polyimides Synthesized and Characterized in this Research

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VITA

Isaac Vincent Farr, son of James W. Farr and Aletha L. McCorquodale (formally Farr), was born on November 9, 1972 in West Covina, California. He was raised in Chino Valley, Arizona, before moving to Lompoc, California, and graduating from Lompoc Senior High School in June of 1990. During his high school years and continuing to the present, his step-father, Thomas A. McCorquodale, has had a profound influence on his life. Isaac has four brothers, Matthew, Sean, Ryley and Tommy, and two sisters, Jamie and Hannah, all of whom bring great joy to his life. In March 1995, he received a B.S. in Science from Oregon State University in Corvallis, Oregon, where he developed an interest in polymer science under the guidance of Professor Richard W. Thies. While at O.S.U., he had the privilege to work alongside Professor Michael M. Lerner and Dr. Christopher O. Oriakhi on nanocomposite materials.

In the fall of 1995 Isaac began graduate studies in the Department of Chemistry at Virginia Polytechnic Institute and State University under the supervision of Professor James E. McGrath. In the summer of 1997, he worked with Sanjay G. Charati and Richard W. Ubersax at Membrane Separation Systems, DuPont Air Liquide (Medal), Newport, Delaware. His graduate research efforts at Virginia Tech focused primarily on the design and synthesis of novel polyimide systems for selective gas separations.

He has accepted a materials development engineer position in the Inkjet Supplies Business Unit at the Hewlett Packard Corporation in Corvallis, Oregon.